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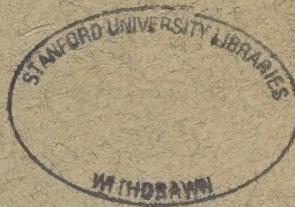
CATALYTIC SAPONIFICATION OF OILS AND FATS

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE
SCHOOL OF THE OHIO STATE UNIVERSITY

BY

CHEH-YAO CHANG, B. S., M. A.



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Dissertation

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I. INTRODUCTION

Recalling Ostwald's statement that there is probably no reaction which cannot be influenced catalytically, and no substance, whether elementary or compound, which cannot act as a catalyst, we should not be surprised that the saponification of oils and fats can be effected catalytically.

A true case of saponification would be to effect the splitting of the oils and fats into free fatty acids and glycerine with alkalies. The alkali and the fatty acids combine to form corresponding salts. Process of hydrolysis, that is to say, the process of resolution of a compound into two products with the simultaneous introduction into the resulting compounds of the component hydrogen and hydroxyl groups of water, have long been known to be sensitive to catalytic acceleration, e. g. the hydrolysis of ethyl acetate and the inversion of cane sugar.

Hydrolysis of oils and fats by water alone is perfectly possible, though, slow in practice. On the other hand, in presence of small quantities of alkali or acid, hydrolysis may be completed in comparatively short time. The technical processes concerned with the use of alkalies may be divided into two kinds: (a) saponification with the aid of alkaline earths and (b) saponification with the aid of caustic alkalies; while those concerned with the use of acids have led to two distinct technical processes, the so-called Acid Process and the Twitchell Process. All these processes are more or less catalytic. But owing to the simplicity in apparatus and operations of the Twitchell Process, its low capital cost of the plant and its working at the atmospheric pressure, it is mainly utilized in this work.

In general, the Twitchell Process of saponification of oils and fats consists first in the removal of foreign impurities occurring in the fatty materials by boiling with sulfuric acid of the strength of 60°.Be. The fatty material is transferred to wooden tanks with tightly fitting cover and then mixed with about half its weight of water to which is added 1 to 2% of the catalytic reagent and an equivalent quantity of an acid. The mass is then thoroughly agitated by blowing live steam through the system from perforated coils in the tanks for 12 to 24 hours. After the end of this time, the glycerine water is settled and withdrawn. About 20% of fresh water is then added, together with a small quantity of sulfuric acid and a second boil is continued for a certain length of time (12-24 hours), after which the emulsion is destroyed by the addition of dilute sulfuric acid. Two layers separate, the fatty acids in the upper and the glycerine in the aqueous layer below. (Martin-Ind. Chem., Organic; p. 93, 1920 Ed.)

Superficially, the process seems to be a rather simple one, as only a very small amount of the reagent together with steam is required to cause nearly complete saponification. But it is far from

being simple as the fatty acids thus obtained readily darkens on exposure to air and at best the process requires a considerable time for practical completion. (Lewkowitsch-Chem. tech. and anal. of oils and fats; vol. 3, p. 248; U. S. P. 1,058,633.) Furthermore, in the preparation of soap stock fatty acids, the full time required for the completion of the hydrolysis is usually not allowed, owing to the fact that the longer the time it is carried out, the darker the product. Again the necessity of preventing serious discoloration has led to the practice of reducing the quantity of the reagent to less than 1%, as it was found that the larger the quantity of the reagent used, the deeper colored became the product (Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes, vol. 3, p. 292 U. S. P. 1,058,633). Both factors contribute materially to reducing the amount of fatty acids obtained. Moreover, the percentage of acid, the percentage of water used at the start, the influence of temperature and the question whether two boils (as they are called) are necessary, etc., still need much study.

So far as is accessible, no description of a systematic series of experiments with the Twitchell Process is recorded. An investigation in this field seems, therefore, very desirable both from a theoretical and a technical standpoint. The successful development of a process of saponification which would produce light-colored fatty acids in a reasonably short time would be of very great practical interest.

The main object of this paper is to obtain information leading to a better knowledge of the working conditions governing the saponification of fatty oils and fats with the reagent along the line of the Twitchell Process and to furnish an index of how the oils will behave in this process of hydrolysis. Another important phase of this study is to find some way to accelerate the reaction so that the time of saponification can be materially shortened. The behaviour of different oils and fats when subjected to this process of saponification is also studied to a certain extent.

Attention should here be called to the fact that many kinds of reagents along the line of Twitchell's have been prepared and put on the market under confusing trade names. In the literature, it is not uncommon that the trade name only is given. So, as far as possible, the composition or the scientific name of the reagent (or at least the substances from which it is prepared) is given in the following pages, as different reagents, of course, give different results.

The reagent worked upon principally in this paper was obtained through the courtesy of the Twitchell Process Co., Cincinnati, Ohio, under the name of "*Liquid Kontakt Saponifier*," which is supposed to be a mixture of mineral oil sulfonic acids obtained from the sludge from purification of mineral oil distillate by conc. sulfuric acid for lighting purposes. The details of the investigation and the results obtained are recorded and discussed below.

II. REVIEW OF THE LITERATURE

The investigation of the Twitchell Process has been of two different characters: (a) the study of some reagents and the preparation of new ones and (b) the study of the operations of the process proper; they are therefore reviewed separately.

The Reagents

The Twitchell Process derives its origin from the so-called "*Acid Process*." The action of sulfuric acid as a hydrolytic agent was first described by Cornett in 1777 (Redeal and Taylor-Catalysis in theory and practice, p. 270, 1919 Ed.; Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes, vol. 1, p. 83, 1913 Ed.). In an investigation of the catalytic rôle of sulfuric acid in the hydrolysis of oils and fats, Twitchell observed that sulfur compounds produced by the action of the conc. sulfuric acid upon the fats or oils might be separated from the fatty material by suitable methods of extraction and could readily be identified as sulfonic acids. To such acids Twitchell attributed the catalytic properties observed in the Acid Process of hydrolysis. Accordingly, he prepared sulfo-acids of the fatty acids, such as sulfo-stearic acid (U. S. P. 601,603, Brit. P. 4, 741) and such reagents were the reagents first employed by him for the hydrolysis. These quickly decompose at 100° C and so cannot be advantageously used (U. S. P. 628,503). Later, the accidental discovery of aromatic-sulfo-fatty-acids yielded the reagents which have been put to practical use in the separation of fatty acids and glycerol. The original aromatic-sulfo-fatty-acid was made by treatment of a mixture of benzene and commercial oleic acid with an excess of sulfuric acid. On pouring the mass into water, an oily layer of the desired product resulted (U. S. P. 628,503). Instead of benzene, phenol or naphthalene may also be used (Journ. Am. Chem. Soc. 1900, p. 22), the latter being used with oleic acid in the manufacture of commercial reagent.

The composition of the reagent was stated by Twitchell (loc cit) to be $C_6H_4 \cdot (HSO_3) \cdot (C_{18}H_{35}O_2)$, $C_{10}H_6 \cdot (HSO_3) \cdot (C_{18}H_{35}O_2)$ and $C_6H_5 \cdot (OH) \cdot (HSO_3) \cdot C_{18}H_{35}O_2$ in the case of benzene, naphthalene and phenol respectively.

Lewkowitsch (Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes, vol. 1, p. 86) made a series of experiments with aromatic-sulfo-fatty-acids prepared from naphthalene, anthracene and phenanthrene respectively, and found that the reagent prepared from naphthalene was much more effective than those prepared from anthracene or phenanthrene.

In 1913, Connstein and von Schönthan of the Verein. Chem. Werke (C. A. 1913, p. 2696; U. S. P. 1,058,633) patented a similar reagent under the name of "*Pfeiling*." This reagent was said to overcome the drawback of discoloring the fatty acids by Twitchell's aromatic-sulfo-fatty-acids, and was made by mixing together 100 parts hardened castor oil with 100 parts of naphthalene and introducing the mixture gradually with constant stirring into 400 parts

of sulfuric acid of 66°Be, the temperature being kept not above 20° C. The reaction mixture is stirred until homogeneous and is poured into 800 parts of water at room temperature, the oily layer containing the reagent forms the upper layer.

G. Petroff (U. S. P. 1,079,437) in the same year also patented a reagent made by sulfonating crude petroleum or its distillate with sulfuric acid. The sulfonated petroleum hydrocarbons are washed with an aqueous lye after the deposition of the precipitated tar layer (Goudron layer). The sulfonic acids thus formed pass over in the form of salts into the aqueous solution which is treated with benzine or benzol to remove the hydrocarbons carried over. The aqueous solution is then decomposed by mineral acid, by which the free sulfonic acids are obtained as a thick, hygroscopic, resinous mass. The latter can further be purified by dissolving in ether or benzol and evaporating off the solvent. The composition is not known and is said to be a mixture of various sulfonic acids of cyclic hydrocarbons of high molecular weight.

Petroff (U. S. P. 1,987,888) in 1914 improved his method of extracting sulfonic acids by treating the upper layer of the sulfonated mixture with dilute alcohol, wood alcohol or acetone, the lower layer being first treated with water to remove the excess of sulfuric acid and then with gasoline or kerosine to obtain the sulfonic acids which are again purified by dilute alcohol, wood alcohol or acetone.

Akt. Ges. zur Erzeug. und Anwend. v. Naptha-sulpho-sauren "*Kontakt*" (C. A. 1916, p. 288; B. P. 17,478) patented a similar process for obtaining sulphonic acids by sulphonation from paraffin or mineral oils, such as solar paraffin and anthracene oils from the tar of lignite, coal, peat or bituminous mineral, the sulphonic acids being dissolved out by dilute alcohol.

During these years, Twitchell made an improvement on his naphthalene-sulpho-fatty-acids by making the pure salts of them, free from all the by-products of sulphonation. The crude naphthalene-sulpho-fatty-acids as first obtained are washed repeatedly with a common salt solution to remove sulphuric acid and aromatic sulphonic acid (U. S. P. 1,170,468; and 1,082,662) and then treated with naphtha or other solvent which dissolves fats or fatty acids not acted upon, the aromatic-sulpho-fatty-acids being left pure. This viscous mass is dissolved in a large quantity of water and precipitated with a salt of such a metal as will form an insoluble compound with the aromatic-sulpho-fatty-acids, such as the barium, magnesium, aluminium, etc. The precipitate, which sinks to the bottom of the vessel, is removed and dried.

Sudseldt and Co. (C. A. 1914, p. 3130; Fr. P. 463,912) patented a similar process for obtaining the metallic salt of naphthalene-stearo-sulpho-acid by precipitating with either BaCl₂ or AlCl₃.

This salt of the aromatic-sulpho-fatty-acid has to be used together with some mineral acid such as sulphuric acid in order to liberate the free sulphonic acids which are active in the hydrolytic process. From this relation, the so-called "*Twitchell double rea-*

gent" (C. A. 1914, p. 2077) often found in the literature may have derived its name. This salt may also be treated with acid and the free sulphonic acid used. It is said to be more effective and less discoloring, as the reagent is in a more concentrated form and is freed from all other impurities.

S. Zipser (C. A. 1914, p. 2077) studied both Twitchell's naphthalene-sulpho-fatty acid and its barium salt and also "*Pfeilring*," the similar reagent made from hardened oil, and obtained good results in less time and with less reagent. Since the original article is not accessible, the information about the length of time and the percentage of the reagent used is therefore not available.

G. Koenig (C. A. 1915, p. 2461) compared two different saponifiers under the name of "*Kontakt*" and "*Pfeilring*." The "*Kontakt*" is said to require more sulphuric acid for its activity than "*Pfeilring*," and the "*Kontakt*" to be more active at the start. The color of the fatty acids obtained is said to be about the same.

Twitchell attributed the action of naphthalene-sulpho-fatty-acid to its solubility in water and again to the fact that its aqueous solution dissolves fatty bodies, acting as a soap solution (Journ. Am. Chem. Soc. 1906, p. 196). At the same time, its solution is strongly acidic and highly dissociated. He showed also that a soluble glyceride like triacetin can be hydrolysed by either dilute mineral acid or naphthalene-sulpho-fatty-acid; but an insoluble glyceride like triolein is not appreciably hydrolysed with the former, while with the latter, the hydrogen ions are as active as they are with triacetin. Moreover, dilute HCl of the same strength as that of naphthalene-sulpho-fatty-acid has the same hydrolysing power on soluble glycerides, but on insoluble glycerides, dil. HCl has practically no effect.

E. Grimlund (Zeits. Angew. Chem., 1912, p. 1326) considered the action of the Twitchell's reagent to be twofold; namely, emulsifying and splitting (hydrolysing). He thought that the reagent consists of two parts; the one, insoluble in salt solution and of complicated composition, does the work of emulsifying; while the other (most probably a sulphonic acid) does the work of hydrolysing; as when the material containing the reagent is washed with NaCl solution until free from acid, the resulting product will still emulsify but will have no other action, and if a small quantity of conc. mineral acid is added, it again becomes active.

Referring to this phenomenon, the writer is of the opinion that, assuming the formula $C_6H_4 \cdot (HSO_3) \cdot C_{17}H_{34} \cdot COOH$ of this reagent as given by Twitchell is correct, when the compound is treated with NaCl solution, a salt of the formula $C_6H_4 \cdot (NaSO_3) \cdot C_{17}H_{34}COOH$ is formed, which naturally loses its hydrolysing property as there are then no highly ionised H-ions which are essential to the hydrolysis. On the other hand, the radical $C_{17}H_{34}COOH$ is not influenced by so treating, so the emulsifying property is not destroyed which is chiefly due to the fatty character conferred by this radical.

F. Goldschmidt (Chem. Ztg., 1912, p. 877-8) referred the activity of the Twitchell's reagent to be due to the free sulphur in the compound, acting catalytically and as an emulsifier Lewkowitsch

(Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes vol. 3, p. 248, 1915 Ed.) explained the action of the reagent by its power of emulsifying and was of opinion that during the steaming of oils or fats, H_2SO_4 is generated, as it were, in *statu nascendi*, and this acts on the glycerides with the formation of sulpho-compounds which are more readily hydrolysed by water than are the glycerides themselves.

J. Grosser (C. A. 1914, p. 3129) extracted the Twitchell's reagent with petroleum ether and showed that the greater the amount that is soluble, the greater will be the activity of the reagent.

Quite recently in 1919 and 1920, R. E. Divine, Assignor to the Twitchell Process Co., Cincinnati, Ohio, Patented a process for obtaining mineral oil sulphonic acids from mineral oil sludge (U. S. P. 1,303,779; and U. S. P. 1,319,027). The process consists of (a) treating mineral oil distillate with SO_3 , (b) treating the formed sludge with one half or twice its amount of water, (c) precipitating the dark solution thus extracted with lime, (d) filtering the CaSO_4 thus formed and (e) salting out the sulphonic acids with NaCl . These sodium salts of mineral oil sulphonates are characterized by being soluble in water, of a light yellow color, and as a plastic, sticky, neutral body.

An alternate process of producing the same is to (a) dilute the sludge with heavy petroleum distillate to free the sludge from the oil and the oil soluble mahogany acids, (b) to add water and boil to separate the heavy H_2SO_4 and (c) to convert the sulphonic acids and H_2SO_4 into their respective sodium salts. The solution containing the sodium mineral oil sulphonates is then extracted with naphtha to free from any oil remaining, the solution being next treated with H_2SO_4 to obtain the free sulphonic acids. This forms the greenish upper layer.

R. E. Divine (U. S. P. 1,330,624) later improved the aforementioned process by salting out with CaCl_2 instead of NaCl to obtain calcium salt of the sulphonic acids.

The reagent obtained from the Twitchell Process Co. is most probably this latter preparation under the name of "*Liquid Kontakt Saponifier*" to distinguish from the "*Solid Kontakt Saponifier*", an alkaline earth salt of the Twitchell's original naphthalene-sulpho-fatty-acids once placed on the market.

The Process

Besides Twitchell who described his original process, B. F. Reuter appears to be the one that has worked in this field. He patented an improved process in using Twitchell's naphthalene-sulpho-fatty-acid-salt (U. S. P. 1,068,079). According to his improvements, the oil or fat is first treated by an acid wash (as it is termed) with 0.5 to 2% 60°Be H_2SO_4 for the reason that it was thought, when the oil is thus treated, hydrolysis seems to be induced to go on much faster. To the washed fat or oil, after settling and separating, is added about 40% water and the mix-

ture brought to a boil. One tenth of the Twitchell's naphthalene-sulpho-fatty-acid-salt is then added, whereupon the contents of the tank are kept at a temperature of 212° F and agitation started. No acid is added, but the acidity of the contents is kept at about 0.05%. The contents are boiled for about an hour with agitation. After this time, the temperature is reduced to about 200-212° F and agitation is stopped, temperature being thus maintained at 200-212° F for 18 hours. At intervals, the contents are brought up to 212° F for a few minutes at a time; in like manner, the agitator is set in motion for 10-30 minutes at a time.

It was claimed that the recurrent raising of the temperature of the contents and the intermittant agitation aid the decomposition. It was also claimed that any increase in temperature and pressure would tend to effect a recombination of glycerine and fatty acids, especially near the final stage of the decomposition.

A second and a third boil are given after every 18 hours with the addition of 0.1% of the reagent and 30% of water, keeping the acidity to about 0.05%.

In 1917, Reuter modified his process by using only 20-30% of water and 0.03-1% acidity (U. S. P. 1,279,485; U. S. P. 1,248,402). He further stated that agitation during the entire boiling operation is more effective than only during a portion of the time, using a temperature of 212° F.

Experimental

In brief outline, the Twitchell process consists of boiling purified oils or fats with water and a relatively small quantity of H_2SO_4 in the presence of a catalyst, which enables the acid and water to react with the fatty materials, setting free the fatty acids and glycerine, which dissolves in the water and is separated at the termination of the operation by drawing off the aqueous layer.

In this work, the original procedure was essentially adhered to, except that the hydrolysis was not carried out continuously without interruption due to some other work at hand. This necessary interruption should have some influence on the length of time, as it takes some time to heat up the cold mixture, every time the operation is renewed. The oil or fat to be hydrolysed was first heated to boiling with live steam, then 1 or 2% 60°Be H_2SO_4 was added and the steaming continued for two hours. The washed oil or fat was settled over night and the clear fatty layer was separated in a separatory funnel. The washed oil or fat was contained in a 500cc round bottom flask provided with a cork having three holes, through one of which there is a stirrer driven by a motor, through the other, live steam can be passed by a perforated bent glass tube; while the third is the exit for the steam. The oil was mixed with the proper quantity of the reagent used, 60°Be H_2SO_4 , and the proper amount of water; and the mixture was stirred up while steaming. After about 24 hours, the glycerine water was settled and withdrawn, 15% fresh water together

with 0.25% 60°Be H_2SO_4 being added to the fat and the boiling resumed through a second period of 20-24 hours, during which the decomposition will proceed to about 95% or higher. The above procedure was followed throughout this work except otherwise specified.

The oil used in this study is cottonseed oil of a "Choice winter pressed" grade, obtained from Southern Cotton Seed Oil Co. The oil is a purified commercial product, having a clear yellow color and practically no odor. Its acid value and saponification value is determined to be 1.7 and 191.4 respectively by the methods given in Lewkowitsch (Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes, vol. 1, 1913 Ed.; p. 379 and 437). The steam used is from a steam pipe or generated in a glass flask when necessary; the 60°Be H_2SO_4 is made by diluting the conc. H_2SO_4 to the proper strength. The reagent used was obtained from the Twit-chell Process Co., Cincinnati, Ohio, under the name of "*Liquid Kontakt Saponifier*," the real composition of which is not publicly known. It is, however, supposed to be a mixture of sulphonic acids of petroleum hydrocarbons recovered from mineral oil sludge (U. S. P. 1,303,779; U. S. P. 1,319,027 and 1,330,624).

The method used to ascertain how far saponification of the oil has proceeded in the progress of the reaction was that given by Lewkowitsch (Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes, vol. 1, 1913 Ed.; p. 636). In brief, the method is as follows: A conveniently large—not weighed—sample is taken and in one and the same sample the number of cc of normal alkali required for the neutralization and saponification values respectively is determined. Supposing a and b be the numbers

$$a \times 100$$

found, then $\frac{a \times 100}{b}$ gives the proportion of free fatty acids. This

method was chosen on account of its convenience when a large number of determinations had to be made. The method was checked with other method using weighed samples.

III. PRELIMINARY STUDY OF THE REAGENT "LIQUID KONTAKT SAPONIFIER"

Before taking up in detail, it is desirable to have a preliminary study of the reagent, so that a better knowledge of it may be obtained. This reagent is a dark, opaque, viscous liquid, very soluble in ether, petroleum ether and water, in which it forms a colloidal solution. It froths on shaking and possesses a detergent property just like a soap solution. It also dissolves in most of the organic solvents like benzene, benzin, chloroform, etc. It is precipitated out, however, from its aqueous solution as dark viscous liquid on standing by mineral acids and metallic salts as BaCl_2 , $\text{Al}_2(\text{SO}_4)_3$, etc.

When treated with absolute alcohol, two parts were obtained, the one, soluble, while the other was insoluble in it. The insoluble

part amounted roughly to 20%. The alcohol-soluble part became a little less soluble in cold water, but readily soluble in hot water.

It was thought that this reagent, being a mixture of sulphonic acids of saturated and unsaturated hydrocarbons, may therefore be hygroscopic and absorb moisture or O_2 on account of the unsaturation. This was not found to be the case as shown by the following determinations:

	1st weighing	2nd weighing	3rd weighing
Wt. of sample:	0.4482gms.	0.4480gms	0.4480gms.

The sample was weighed after every two days' exposure to air.

The reagent is acid towards methylorange and phenolphthalein. It seems to contain two types of acid group; one of which is a strong acid type, while the other, that of a weak acid. The acidity can first be titrated with alkali in presence of methylorange as an indicator and then titrated with phenolphthalein.

As a thorough investigation is intended, this examination of the reagent will be of much help to the further study, as will be seen in the subsequent pages.

IV. PREPARATION OF THE TYPICAL CATALYTIC REAGENTS AND A COMPARISON OF THEIR ACTIVITY

As mentioned above, Twitchell's reagent has been modified by him and other investigators many times since its first appearance. It will be interesting to prepare a few typical ones of its kind and to make a comparative study of their activity in connection with the study of the one at hand. Accordingly, two typical compounds were prepared and the "*Liquid Kontakt Saponifier*" now worked on forms the third type.

a) *Barium salt of the naphthalene-sulpho-fatty-acid.* The original Twitchell reagent was made from commercial oleic acid and conc. H_2SO_4 ; and the product was called *sulpho-fatty-acid* (U. S. P. 601,603). This reagent was soon replaced by a new and more active reagent made by treating commercial oleic acid and naphthalene with conc. H_2SO_4 and was called *naphthalene-sulpho-fatty-acid* or *naphtho-stearo-sulphonic-acid* (U. S. P. 608,503; Journ. Am. Chem. Soc. 1900, p. 22; Ibid 1906, p. 196). The latter reagent was claimed to saponify oil or fat in from 8-10 hours, using less than 1% of the reagent.

This was afterwards found to contain as impurities, about 35% of oleic acid, 25% of water containing H_2SO_4 and naphthalene sulphonic acid and could be concentrated by forming its metallic salt. It was claimed that the salt of the compound has double the strength of the original product (U. S. P. 1,170,468).

So the reagent was prepared as follows: To the commercial oleic acid were added slowly and with shaking 40 parts of its weight of naphthalene and then an excess of conc. H_2SO_4 . After standing for several hours, water was added and the excess of

the H_2SO_4 washed out; the resultant compound being deposited on the top in the form of an oil which was separated and removed. The oily product was treated with water and heated to boiling. The upper layer of dark, viscous oil was repeatedly washed with water containing HCl , and was then washed a number of times with gasoline, which dissolves the unacted fatty matters and naphthalene, leaving the desired compound pure, which was then dried at 100°C to remove traces of HCl and water. This was then concentrated by treating with a solution of common salt to wash out the greater part of the H_2SO_4 and naphthalene sulphonic acid. This treatment converts also part of the naphthalene-stearo-sulphonic-acid into its salt. The material was then extracted with naphtha to dissolve the fats and fatty acids unacted upon. The extracted material was then dissolved in a large quantity of water and precipitated with BaCl_2 in the form of the barium salt of the naphthalene-stearo-sulphonic-acid, which sank to the bottom as a dark, viscous mass. The compound became tough when dried.

b) Naphthalene-sulpho-fatty-acid from hardened oil and its salt—(Pfeilring).

Another modification of the Twitchell's original reagent was made by H. von Schoenthan of Schoenberg (U. S. P. 1,058,633). He treated, instead of unsaturated oleic acid, hardened castor oil with naphthalene and sulphuric acid. The reagent was claimed to effect complete saponification in 6-8 hours, using 0.2% of the reagent.

In preparing naphthalene-sulpho-fatty-acid from hardened oil, hydrogenated cottonseed oil obtained by passing hydrogen through the oil for 5 hours in presence of nickel catalyser was used. To the hardened cottonseed oil was added 100 parts of naphthalene and treated with an excess of conc. H_2SO_4 , added slowly with stirring. The temperature was kept below 20°C . The stirring was continued until the mixture was homogeneous, whereupon the whole mass was introduced into 800 parts of water at room temperature and well stirred. Two layers were soon formed and the upper dark, viscous layer was separated and freed from the impurities by washing with a solution of common salt, extracting with naphtha to dissolve the unacted fats and the residue dissolved in a large amount of water and precipitated with BaCl_2 solution. The barium salt was obtained as a dark, viscous mass with a slightly lighter color than that of the naphthalene-stearo-sulphonic-acid from unsaturated oleic acid.

c) Liquid Kontakt Saponifier or mineral oil sludge sulphonic acid.

This reagent was obtained directly from the Twitchell Process Co. as mentioned above.

Having obtained the three principal modifications of the catalytic reagent, it will be interesting to make a series of experiments with equal amounts of each of these reagents and a comparison of

their activity. The experiments were made under like conditions with the exception that the reagent used was different in each case. The charge consisted of the following:

100 parts cottonseed oil
1 part reagent.
40 parts water.
1 part 60° Be H₂SO₄

and was twitchellised with live steam. The results are shown below and in the accompanying curves (Fig. 1).

TABLE 1—A COMPARISON OF THE ACTIVITIES OF 1% OF THE DIFFERENT REAGENTS IN THE HYDROLYSIS OF COTTONSEED OIL
PERCENTAGE OF FATTY ACIDS

Time in Hours	a*	b*	c*
	Exp. 1	Exp. 2	Exp. 3
0	1.5	1.5	1.5
4	8.8	5.7	55.0
8	26.9	24.2	70.5
16	41.5	60.8	81.7
24	46.7	77.5	86.6
32	51.3	84.8	92.3
40	53.0	88.2	93.1
44			94.1
46			94.6
48	55.0	89.7	94.9
50			95.0
52			94.9
54			95.0

* a=Barium naphthalene-stearo-sulphonate; b=Barium salt of naphthalene-sulpho-fatty-acid from hardened cottonseed oil; and c=Liquid Kontakt Saponifier.

These results indicate that the reagent from hardened oil has a rate of cleavage higher than that of the reagent from the unsaturated oleic acid. The color of the fatty acids obtained is lighter too. It should be noted that the reagent from oleic acid is more active at the start, thus confirming Koenig's observation (C. A. 1915, p. 2461). During the experiments, it was observed that good emulsion was formed in both cases; but after 6 hours, the color of the reagent from the oleic acid was much darker than that of the reagent from hardened oil as appeared in the emulsion.

Ellis stated (Ellis-Hydrogenation of Oils-1914 Ed. p. 28) that the rate of a saponification with the hardened oil product "Preilring" is approximately that of the Twitchell reagent. Using equal parts of the two reagents under like conditions the following results were obtained:

	5 hrs.	23.25 hrs.	34 hrs.
	% of fatty acids		
Twitchell reagent	37.23	83.31	88.94
Pfeilring reagent	36.92	80.18	88.69

As the actual quantity of the reagents used were not given, the results are incomparable.

From these results, it will again be seen, that these two reagents are not able to effect complete saponification in 6-8 hours, using 1% of the reagent, as they were claimed to. (Journ. Am. Chem. Soc. 1906, p. 196). Concerning these statements, as was

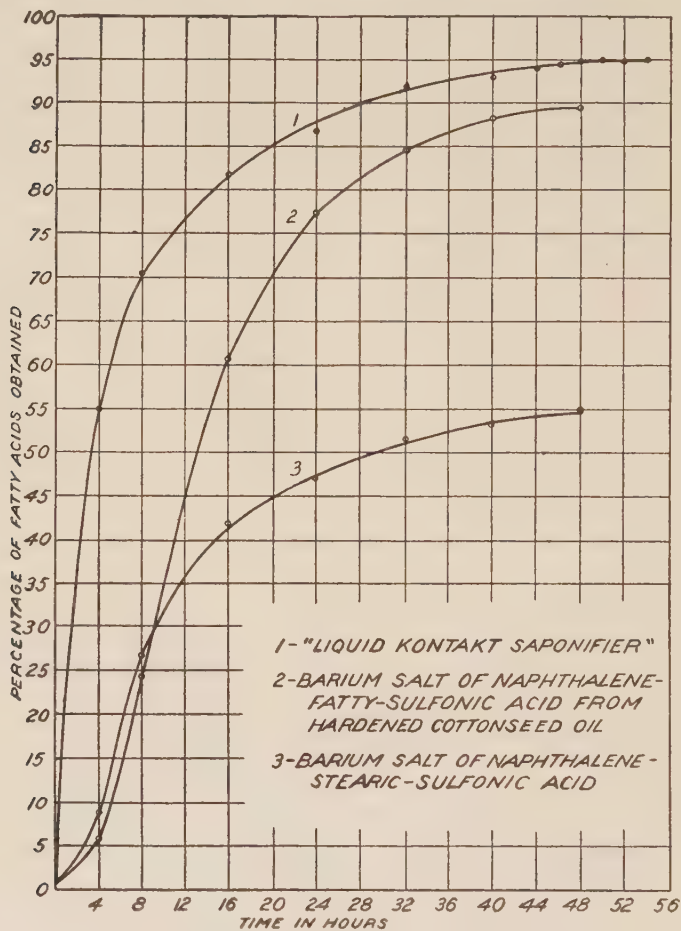


FIG. 1. COMPARISON OF THE EFFICIENCY OF THREE DIFFERENT REAGENTS

mentioned before, no description of a systematic series of saponification experiments with actual data is recorded so far as is accessible. The new "Liquid Kontakt Saponifier," supposed to be the most efficient saponifier at present, was claimed to effect saponification of 95% or higher in 48 hours, using three-fourth to one % of the reagent (The Twitchell Process, p. 13 and 15). This was confirmed by the above results. This reagent is far more efficient

in splitting activity than the Twitchell's naphtho-stearo-sulphonate, and is also more active than that from the hardened oil. It has no discoloring effect on the fatty acids in spite of its dark color. It is further investigated in the following pages.

V FACTORS INFLUENCING THE PROCESS.

As mentioned above, the actual practice of saponification of fats or oils by Twitchell process are influenced by many factors, although in general, it consists of boiling the fats or oils with water and a relatively small quantity of H_2SO_4 in the presence of a catalyst. In the present investigation, the various factors which came into play are studied in detail.

(a) Effect of mechanical stirring:—it is well known that the velocity of a chemical reaction in a heterogeneous system depends to a great extent on the frequency with which the interacting molecules come in contact with one another, i. e. on the interacting surfaces. We also know that oils and water will form two separate layers when brought together and will not intermingle with each other. But in this process of saponification, the oils or fats are hydrolysed by the aqueous acid solution with the assistance of a catalyst.

Therefore, the more intimate, the particles of the oils or fats come in contact with the hydrolysing agent, water, the faster will be the rate of hydrolysis. When the mixture containing the oil and water together with a small amount of H_2SO_4 and the catalyst was twitchellised, it was observed that large globules of oil were formed floating on the water, even on steaming. Although it was claimed, that the reagent, being soluble in water and in oil, assists the reaction in forming emulsions and microscopic particles, thus bringing about more intimate contact with each other, it was, however, found that both the bubbling action of the steam and the emulsifying effect of the reagent were not able to bring about the desired intermixing, unless coupled with the mechanical stirring.

In original Twitchell Process, no stirring devices were provided, as it was thought that the bubbling force of steam from the perforated coil would produce this desired mixing (U. S. P. 601, 603). Reuter devised an apparatus with mechanical stirrer and during the entire process of saponification, the mixture was under constant agitation (U. S. P. 1,068,079). Two experiments were made under like conditions, except in the one case, no stirrer was used, while in the other, constant agitation was maintained. The fact that the mechanical stirring does help the rate of saponification was plainly shown by experiments 3 and 4 and the Fig. 2, though it is more evident at the beginning and only to a slighter extent near the completion of the reaction. The results are recorded below:

TABLE 2—THE EFFECT OF MECHANICAL STIRRING

Time in Hrs.	Percentage of Fatty Acids	
	Exp. 3 (with stirrer)	Exp. 4 (without stirrer)
0	1.5	1.5
2		13.4
4	55.0	
5		43.4
7		51.2
8	70.5	
11		71.1
13		76.5
16	81.7	79.8
20		83.4
24	86.6	86.5
29		90.1
32	92.3	
34		93.9
38		94.1
40	93.1	94.5
44	94.1	
46	94.6	
48	94.9	
50	95.0	
52	94.9	
54	95.0	

The above data were obtained when charges consisting the following:

100 parts cottonseed oil

40 parts water

1 part reagent

1 part 60°Be H_2SO_4

were twitchellised.

(b) Time of steaming—From the data in Table 2 and the accompanying curves in Fig. 2, it will be seen that the percentages of fatty acids obtained increase with the length of time. It is also to be noted that the saponification went on fast at the beginning, e. g., within 12 or 16 hours and slowed down thereafter until about 24 hours, when the glycerine water was drawn off and about 0.25% of H_2SO_4 was therefore added to accelerate the reaction, and a second boil of 16-24 hours given.

During the second boil, the rate of saponification is very slow, usually not over 10% of the oil is saponified in this 24 hours. Especially at the end of the process is the rate of the reaction so slow that no appreciable change takes place. The reaction is usually

considered complete when 95% or over of the oil is saponified, as no appreciable reaction will take place, when such percentages have been reached.

An investigation was made to determine what influence the length of time would have on the progress of the reaction when indefinitely prolonged. The results in experiment 3 showed that

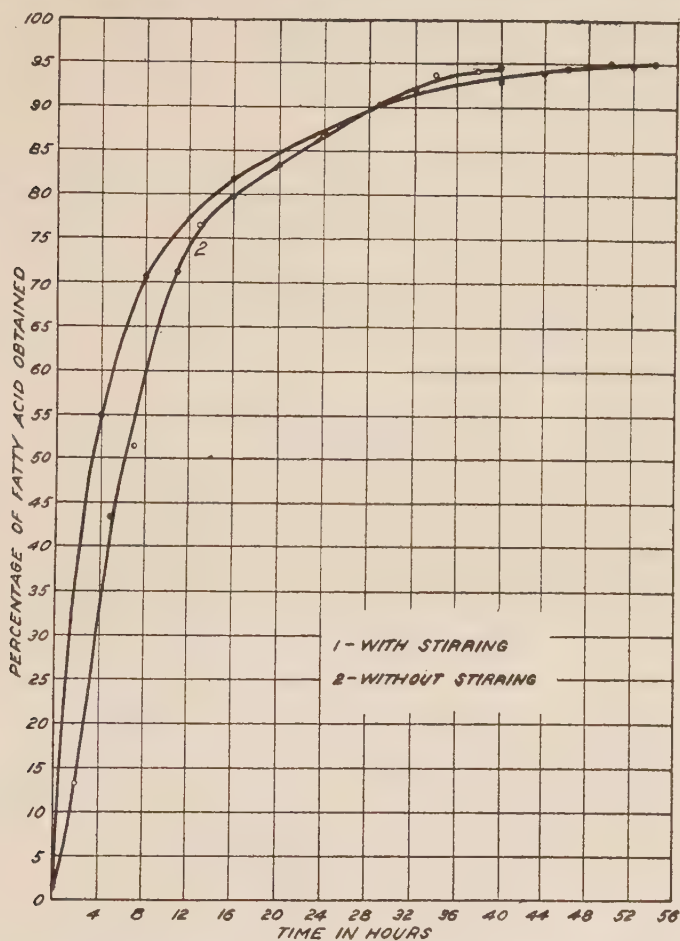


FIG.2. THE EFFECT OF MECHANICAL STIRRING

there was practically no increase in fatty acids over about 95% when the time was further prolonged. This is not surprising when we consider that the reaction of hydrolysis is a reversible one, and near the end of completion, the products of the reaction may be present to such an extent that they react and a recombination continuously takes place and the reaction does not proceed beyond this equilibrium (Lewkowitsch-Chem. Tech. and Anal. of Oils, Fats and Waxes, Vol, 3, 1915 Ed., p. 248). It was observed that the longer

the process is carried on, the darker is the discoloration; this will be shown, however, to be not the case, if air is carefully excluded.

(c)—Amount of the reagent and the discoloration effect—It was claimed that the fatty acids obtained from the Twitchell process readily darken on exposure to air and the product is thus rendered unfit for many industrial uses. It was also claimed that a large quantity of the reagent increases the tendency of discoloration. The necessity of preventing the serious discoloration has led to the practice of reducing the quantity of the reagent to less than 1% (Lewkowitsch-Chem. Tech. and Anal. of Oils, Fats and Waxes, Vol. 3, 1915 Ed., p. 292).

In response to a critical discussion of the properties of soaps made with hardened oils, Audfelt brothers stated that for several years, they had been splitting large quantities of hardened oil by the Twitchell Process and converting the fatty acids into soap and had found these fatty acids to be of good color and the soaps prepared from them to be in no wise lacking in color (Ellis-Hydrogenation of Oils, 1914 Ed., p. 30). From these facts, it will be seen that the discoloration of the fatty acids may be due to some influences other than the reagent itself.

During experimenting, it was observed that the color of the fatty acids became deeper and deeper, the longer the time the reaction was allowed to continue. This was found to be due to the fact that the repeated opening of the flask to allow of a sample to be taken allows the entrance of the air which causes the discoloration of the fatty acids. This was clearly shown by experiments 5 and 6, which were carried out in like conditions with the only difference that, in the one case, the mixture was steamed continuously for 8 hours; while in the other, it was interrupted every two hours to allow of a sample to be taken. The results were as follows:

TABLE 3—INFLUENCE OF THE ACTION OF AIR

Time in hrs.	% fatty acids		Color	
	Exp. 5	Exp. 6	Exp. 5	Exp. 6
2	32.1	-----	very light yellow	-----
4	54.8	-----	very light yellow	-----
6	59.7	-----	yellow	-----
8	65.1	68.3	brownish	very light yellow

An investigation was then made as to what influence the percentages of the reagent used would have on the progress of the saponification. In carrying out these experiments, the quantities of oil, water, H_2SO_4 and other conditions were carefully kept the same, except different amounts of the reagent were used as shown below:

Exp. No.	Cottonseed Oil	Water	H ₂ SO ₄	Reagent	Time to begin 2nd boil after 24 hrs.
7	100 gms.	40 gms.	1%	0.25%	
8	"	"	"	0.5%	"
2	"	"	"	1%	"
9	"	"	"	1.5%	"
10	"	"	"	2%	"
11	"	"	"	3%	"
12	"	"	"	5%	"

The results are recorded in Table 4.

TABLE 4—HYDROLYSIS OF COTTONSEED OIL WITH DIFFERENT PERCENTAGES OF THE LIQUID KONTAKT SAPONIFIER.

Time in hrs.	Percentages of Fatty Acids						
	Exp. 7	Exp. 8	Exp. 2	Exp. 9	Exp. 10	Exp. 11	Exp. 12
0	1.5	1.5	1.5	1.5	1.5	1.5	1.5
3.5	-----	-----	-----	-----	74.5	79.3	-----
4	1.6	1.5	55.0	60.3	-----	-----	87.1
6	-----	-----	-----	82.7	-----	-----	-----
8	1.8	1.7	70.5	84.2	-----	-----	93.4
9	-----	-----	-----	-----	-----	86.0	-----
11	-----	-----	-----	-----	84.5	-----	-----
12	-----	-----	-----	-----	-----	90.4	-----
15	-----	-----	-----	85.9	90.2	91.3	-----
16	2.3	13.0	81.7	-----	-----	-----	-----
18	-----	-----	-----	86.8	-----	-----	-----
20	-----	-----	-----	-----	-----	92.8	-----
21	-----	-----	-----	88.4	-----	-----	-----
24	2.6	34.5	86.6	89.8	92.6	92.8	93.9
28	-----	-----	-----	91.5	-----	-----	-----
30	-----	-----	-----	93.3	-----	-----	-----
32	3.0	38.3	92.3	-----	-----	-----	-----
40	4.1	42.5	93.1	-----	-----	-----	-----
41	-----	-----	-----	95.1	-----	-----	-----
44	-----	-----	94.1	-----	-----	-----	-----
46	-----	-----	94.6	-----	-----	-----	-----
48	5.0	49.3	94.9	-----	-----	-----	-----
50	-----	-----	95.0	-----	-----	-----	-----
52	-----	-----	94.9	-----	-----	-----	-----
54	-----	-----	95.0	-----	-----	-----	-----

From the above results, it will be seen that the rate of hydrolysis can be increased by increasing the percentage of the reagent used. It is especially to be noted that the rate of hydrolysis increases very rapidly at the beginning of the reaction and slows down gradually; the extent of the hydrolysis is not much effected by increasing the amount of the reagent, there is a gradual slowing down in every

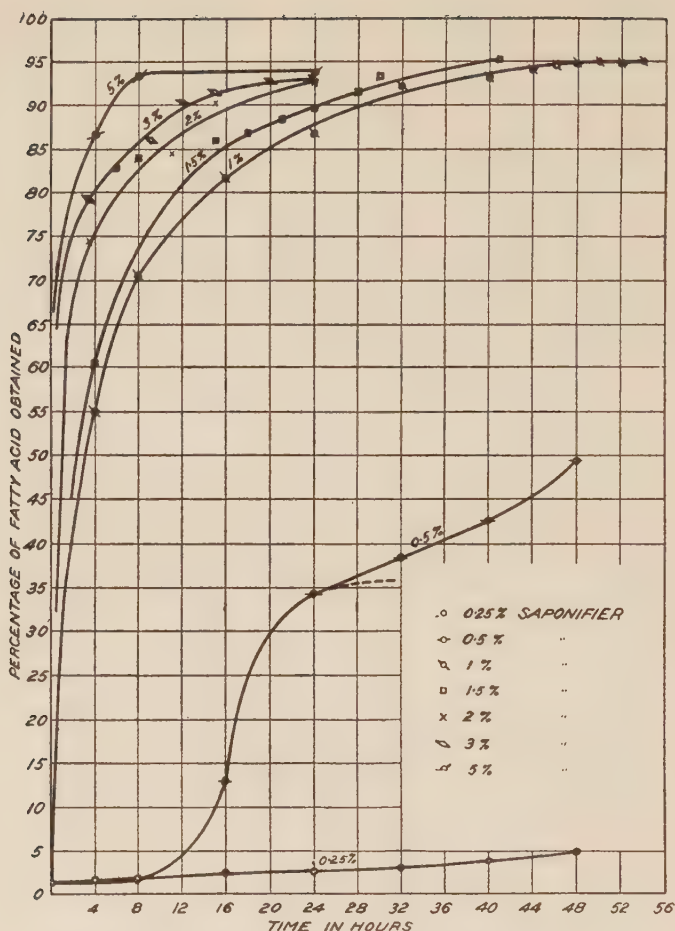


FIG. 3. HYDROLYSIS OF COTTONSEED OIL WITH VARYING AMOUNTS OF LIQUID KONTAKT SAPONIFIER

case. The increase of the amount of the reagent has also an effect to form an emulsion at an earlier stage, which is only formed after 3 or 4 and sometimes 6 or 7 hours' steaming when 1% of the reagent is used. Using 3 or 5%, the emulsion forms earlier and is very persistent; also foaming takes place which would be very undesirable in technical practice. On the other hand, however, the color of the fatty acids obtained was found not effected at all by the increased amount of the reagent when the exclusion of the air had been carefully attended to. In reality, the color of the fatty acids was even slightly better when large percentages of the reagent were used. This was shown by the fact that the color of the fatty acids, even when 5% was used, was perfectly white after

8 hours continuous steaming; and it only became gradually colored with repeated interruption, whereby the entrance of the air could not be prevented.

So with the "Liquid Kontakt Saponifier," the rate of hydrolysis could be increased by using a higher percentage of the reagent without discoloring the fatty acids, if it was not for the other inconveniences encountered in its usage. By using a large amount of the reagent, the persistent emulsion formed is very difficult to break and to separate into two layers, thus giving much difficulty in separating glycerine solution and fatty acids in the subsequent operations.

To get an idea of whether less than 1% of the reagent would effect the complete saponification in a reasonable time, experiments 7 and 8 with 0.25% and 0.5% of the reagent respectively were carried out.

From the results of these experiments, it will be seen that with 0.5% of the reagent, the reaction proceeded very slowly at the beginning, but with increasing speed after 8 or 12 hours and began to slow down in about 24 hours, as shown by the dotted line of the curve (Fig 3). As was usually done, about 0.25% H_2SO_4 was then added to accelerate the reaction, by which another 15% of fatty acids was obtained and until 48 hours, about 50% of the oil is saponified. The time for complete saponification might have to be doubled or more when the quantity of the reagent is halved.

One point to be especially noted is the fact, that it was observed during the experiment, that no emulsion was formed until after 12 hours when emulsion suddenly took place. The percentage of the fatty acids at that time was about 5%. Attention must also be called to the importance of this experiment in showing the fact that even with 1% H_2SO_4 , but with not enough reagent to produce the desired emulsification, hydrolysis cannot proceed at normal speed until enough fatty acids are generated in the system, which, owing to its emulsifying power, might accelerate the reaction to a great extent. This point will be more emphasized in the subsequent pages.

With only 0.25% of the reagent, the reaction proceeded exceedingly slowly, and the reagent did not seem to have any hydrolysing power, as only very thin emulsion was formed during the entire 44 hours' steaming.

In the light of the above experiments, we will see that less than 1% of the reagent will not be able to effect the desired hydrolysis in a reasonable time, although the reaction does proceed when 0.5% is used. As the object of this work was to shorten the working hours which are now necessary, no effort was made to study further in this direction. With reference to the effects of the percentage of the reagent, 1% is considered the most suitable quantity, although less than 3% might also be used, if cost is of minor importance.

(d) Percentage of acid used—The use of the acid is simply to assist the hydrolysis. It is to be understood that with the catalytic reagent alone, efficient hydrolysis cannot be obtained. It is to the combined effect, of the strong acid, highly dissociated, of the

peculiar property of promoting the mutual solubility of the oil and water and of the emulsifying power of the reagent that the efficient hydrolysis is due. Of the mineral acids, either the HCl or H₂SO₄ could be used. Lewkowitsch used the HCl in the study of hydrolysis of oils and fats and found it necessary to add a fresh quantity of HCl after taking each sample, because part of the HCl escaped as gas (Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes; vol. 1, 1913 Ed., p. 79.) Owing to the fact that steam was to be passed through the system in this process, HCl was not used here. H₂SO₄ was used instead throughout this work, not only for its non-volatility, but also for its acting to some extent as an emulsifying agent. The reason for using H₂SO₄ of 60°Be is simply because that the stronger acid will char the oil or fat, thus discoloring it, while H₂SO₄ of the latter strength will not injure.

On account of the lack of the knowledge of how the acid assists the hydrolysis, whether the hydrolysis will proceed without the presence of any acid and whether there is any relation between the amount of the acid used and the discoloration of the fatty acids, experiments with the same amount of the other constituents, constituting the batch, but with the varying quantities of the acid at the start were carried out as follows:

100 parts cottonseed oil

40 " water

1 " reagent

and 0%, 1%, 2%, 4% acid at the start.

It was observed that the experiment with 0% acid at the start had a very good emulsion right at the beginning and the color of the emulsion was perfectly white. It, however, turned yellower only about 24 hours, during which time, air was not prevented due to repeated interruption for taking samples. The experiments with 2% and 4% acid were not as well emulsified at the start, as more and more acid was used. The experiment with 1% acid was emulsified after 3 or 4 hours, while the experiment with 4% acid was apparently not well emulsified. Seeing that, in the last experiment, the hydrolysis went on just as well when no apparent emulsion took place, emulsion, therefore, might not be the only factor by which the rate of hydrolysis could be accelerated; or else, some other factor might have come into play.

The fatty acids obtained, on the one hand, were discolored at an earlier stage with the higher percentage of the acid used, e. g. the color of the fatty acids in experiment with 4% acid became dark after about 8 hours, while the experiment with 2% acid became dark after 16 hours and experiment with 1% acid only became so after about 20 hours. This seems to indicate that there is a relation between the discoloring effect of the air and the percentage of the acid present, as the more acid is present, the faster and stronger seems to be the action of the air. When acid is present to a certain extent, it will have a precipitating effect on the reagent, thus reducing the emulsifying power of the reagent as observed in the above experiments. The precipitation of part of the reagent could

be observed in the case of 4% acid, while in the case of 2% acid the precipitation was not so obvious.

The results showing the extent and rate of the hydrolysis were shown in Table 5 and the accompanying Fig. 4.

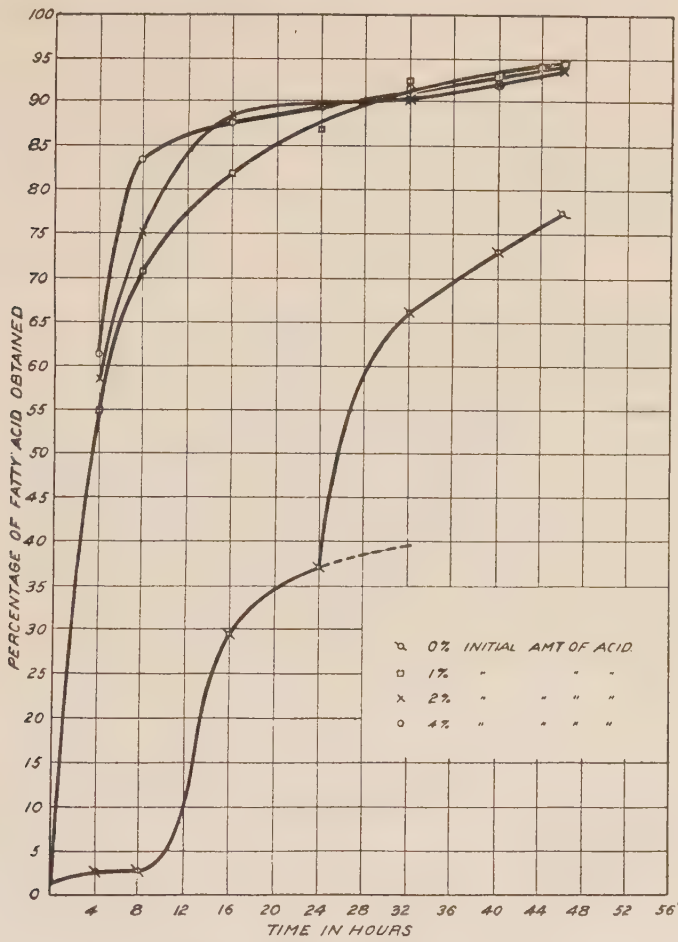


FIG 4 HYDROLYSIS OF COTTONSEED OIL WITH
DIFFERENT INITIAL AMOUNTS OF ACID

TABLE 5—HYDROLYSIS OF COTTONSEED OIL WITH DIFFERENT INITIAL PERCENTAGES OF ACID.

Time in hrs.	Percentage of fatty acids			
	Exp. 13 0% acid	Exp. 2 1% acid	Exp. 14 2% acid	Exp. 15 4% acid
0	1.5	1.5	1.5	1.5
4	2.6	55.0	58.5	61.2
8	2.7	70.6	75.1	83.5
16	29.3	81.7	88.4	87.7
24	36.9	86.6	89.5	89.6
32	65.9	92.3	90.1	91.4
40	73.3	93.1	92.5	92.6
44	-----	94.1	-----	-----
46	77.2	94.6	93.6	94.7

From the above results, it can be seen that both the rate and extent of hydrolysis in presence of acid are larger in comparison with the experiment having no acid at the start. The rate of hydrolysis increases approximately with the increase of the acid present. The extent of hydrolysis, however, is not materially changed by using more acid than 1%. Also a higher percentage of acid than 1% can only accelerate the hydrolysis at the beginning and has little influence near the end of the reaction. A glance of the results will reveal that the action of the reagent in hydrolysis must be co-operated with the acid in order to get efficient results, especially when the results of experiment 13 are examined.

The curve with 0% acid at the start in Fig. 4 is especially interesting in showing the fact that with no acid, the action of the reagent is much less efficient.

This curve suddenly rises after 8 hours and slows down gradually after 16 hours until 24 hours. This may be explained that after steaming for 8 hours, the complex sulphonic acid is decomposed into sulphuric acid in *statu nascendi* as Lewkowitsch assumed (Lewkowitsch-Chem. tech. and anal. of oils, fats and waxes, vol. 3, 1915 Ed., p. 248), and with this acid in nascent form, hydrolysis proceeds to some extent. The curve quickly rises again until 32 hours. It should be noted that after 24 hours when the so-called second boil began, 0.25% acid was added, as was done in every case, which caused this rapid rising. This sudden rise is not so evident at the 24 hour point when acid is present from the start in other cases, although in the other cases, this addition of the small amount of acid does accelerate the rate of the reaction some when it has become very sluggish.

In the light of the above results that the discoloration effect of the air is much quicker and stronger, experiments with much smaller amounts of both the reagent and the acid at the beginning and reserve them for the successive addition after shorter periods

as Reuter suggested (U. S. P. 1,219,485), were carried out. Reuter usually required 54 to 72 hours, 3 boil of 18-24 hours. Our charge consisted of

100 parts cottonseed oil

40 parts water

0.25 part reagent

0.25 part acid

and was twitchellised as usual.

After 8 hours, the mixture was settled and separated, whereby the glycerine water was taken off and 0.25% of the reagent together with 0.04% acid and fresh water were added and the contents were again twitchellised. This operation was repeated after 16 hours and 24 hours, after which only 0.04% acid was added after every 8 hours. The results were shown in Table 6 and Fig. 5.

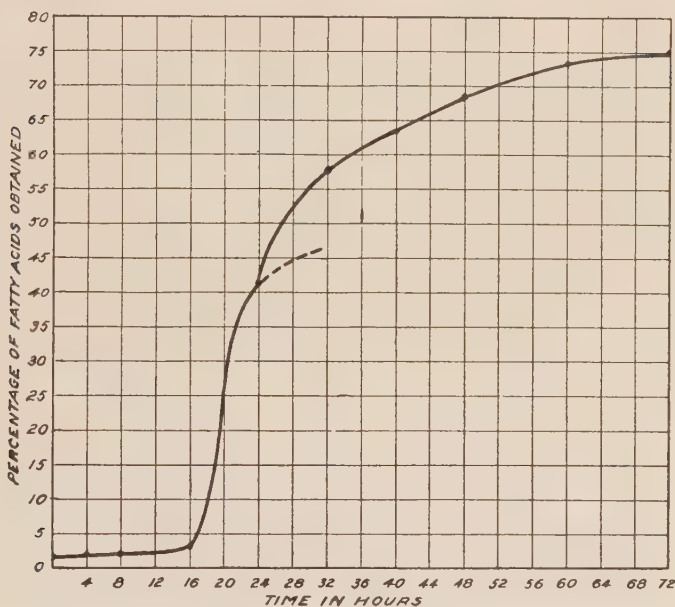


FIG. 5. HYDROLYSIS OF COTTON SEED OIL BY
SUCCESSIVE ADDITION OF REAGENT AND ACID

TABLE 6—HYDROLYSIS OF COTTONSEED OIL BY SUCCESSIVE ADDITION OF REAGENT AND ACID.

Time in hrs.	% fatty acids Exp. 16	Remarks
0	1.5	No emulsion, light yellow oil water mixture.
4	1.7	" " " "
8	1.8	" " " "
16	3.0	" " " "
24	41.2	white emulsion, not discolored
32	57.7	" " " "
40	63.5	" " " "
48	68.6	" " " "
60	73.4	" " " "
72	75.0	" " " "

Reuter stated that the discoloration of the fatty acids could thus be avoided by the successive treatment with smaller quantities of reagent and acid (U. S. P. 1,219,485). Although it has been shown that this reagent has no discoloring effect on the fatty acids if air is carefully excluded, the discoloring action of the air is prominent if a larger amount of acid than 1% is present. With such small quantities of acid (0.04%) added at every 8 hours interval, the fatty acids were found perfectly light in color, much lighter than when a larger amount of acid was used, although the action of the air was not carefully prevented when small amount of acid was used. This agrees with Reuter's statement.

But the experiments fail to show that with successive addition of smaller amounts of reagent and acid (which amounts to a total of 0.49%), the oil could be completely saponified in about 72 hours as claimed by Reuter, although the reagent amounts to 1% at last. The above results showed that it would take much longer time to complete the reaction, as the reaction seems to slow down gradually. This is better seen in the curve in Fig. 5. After 0.5% of the reagent had been added there was no appreciable hydrolysis. Hydrolysis seemed to proceed faster after 16 hours when 0.75% of the reagent had been added with more acid. It then slowed down again as shown by the dotted line at 24 hours, when 0.04% acid was added to accelerate the reaction.

In view of the fact that, although with this successive treatment, the fatty acids were not discoloured, the complete hydrolysis would take too much time; and as the color of the fatty acids was not effected with not more than 1% of acid and exclusion of the air, this successive treatment was considered not necessary.

(e) Percentage of water used—In view of the fact that no matter what quantity of water is used at the beginning of the operation, steam will gradually condense as the operation is continued, it is very important and interesting to see whether the quantity of water used at the beginning has any influence on the

emulsion and the rate of hydrolysis. Accordingly, a series of experiments, using 0%, 20%, 40% and 80% water at the beginning was carried out, keeping other conditions the same, viz.,

100 parts cottonseed oil
 1 part reagent
 1 " acid.

In all these experiments, emulsion was fairly well formed in each case and the color was almost the same. Owing to the steam being condensed more in one case than in another for practical reasons, there was given in Table 7 also the ratio of fat to water at the end of the operation which came to about the same. In reality, the quantity of the water used at the beginning would make the ratio of fat to water vary in the different cases, i. e. the concentration of the glycerine water would be different, but this was changed by the variable condensation. The results were shown below:

TABLE 7—HYDROLYSIS OF COTTONSEED OIL WITH DIFFERENT PERCENTAGES OF WATER AT THE START.

Time in hrs.	Percentage of fatty acids			
	Exp. 17 0% water	Exp. 18 20% water	Exp. 2 40% water	Exp. 19 80% water
0	1.5	1.5	1.5	1.5
4	55.5	38.7	55.0	48.2
8	72.5	63.9	70.6	72.8
16	84.9	86.4	81.7	89.2
24	88.8	89.7	86.6	88.1
32	93.1	93.1	92.3	91.9
40	93.5	94.2	93.1	91.9
44	94.7	94.4	94.1	94.1
Ratio of fat to water in cc	100:150	100:180	100:160	100:180

From the above data, it will be seen that the quantity of water used at the beginning of the operation does not effect very much the rate and extent of the hydrolysis and no absolute failure of the splitting operation should result from the use of too much or too little water. In the above data the hydrolysis after 8 hours is about the same in every case, and in the case of 4 hours and 8 hours, the percentage of fatty acids is about the same in using 0%, 40% and 80% of water at the beginning, except in the case of 20% of water where the percentage of fatty acids obtained is lower.

In general, therefore, the influence of the quantity of water used at the start on the hydrolysis is but little; in practice, however, 40% or 50% of water should be suggested, as 0% water would lead to a persistent emulsion at the start and 80% water would make a fairly large bulk in factory scale, thus unnecessarily diluting the glycerine water.

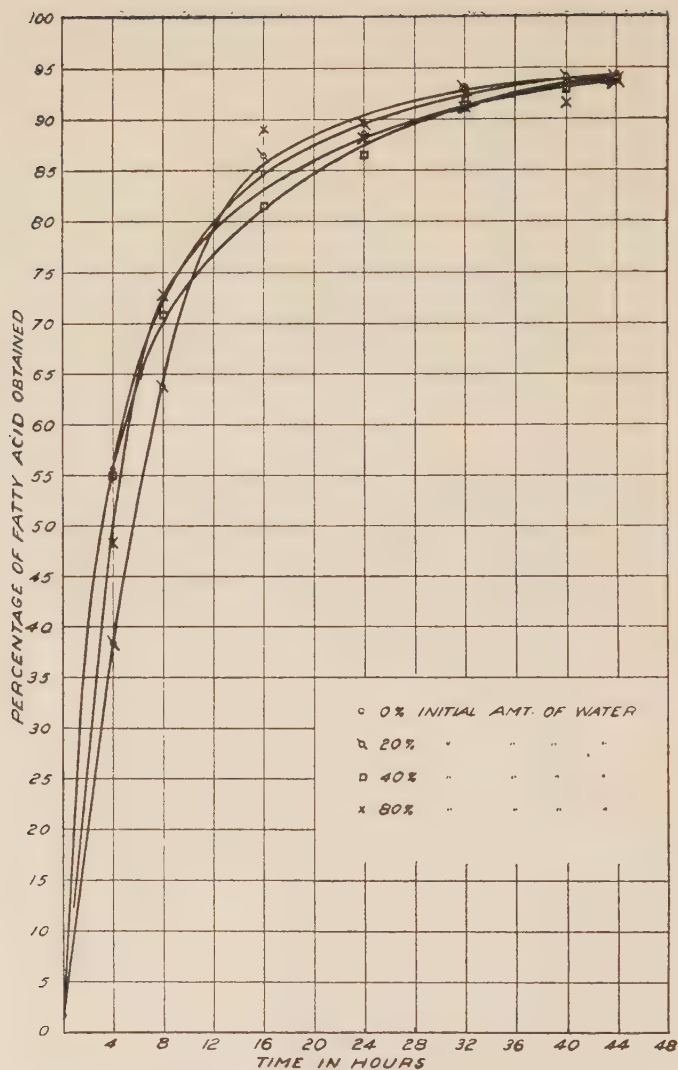


FIG. 6 HYDROLYSIS OF COTTONSEED OIL WITH DIFFERENT INITIAL AMOUNTS OF WATER

(f) Effect of temperature—Twitchell originally used the temperature of live steam to effect the hydrolysis and stated that a higher temperature enough to evaporate the water formed would effect a recombination of glycerine and fatty acids (Journ. Am. Chem. Soc., 1907; p. 566-71; U. S. P. 844,426). Reuter was of opinion that the decomposition was more complete at the low temperature, by which he meant to keep the temperature at 212°F (U. S. P. 1,219,485). He further stated that any increase in tem-

perature would tend to effect a recombination of glycerine and fatty acids to form fat or oil, especially near the final stages of decomposition. In view of the importance of the temperature for any chemical reaction, a series of experiments at various temperature was carried out to find the best temperature suitable for the process.

In this investigation, the flask was heated on a sand bath with a very small flame to keep the steam from condensing too much. This was found necessary on account of using the glass apparatus which cools and radiates heat very rapidly, especially in the winter time. The temperature of the contents of the flask was found to be at 102-103°C and never above 105°C.

These experiments were carried out with the same amount of the constituents, constituting the charge as follows:

100 parts cottonseed oil
40 " water
1 part reagent
1 " acid

and were twitchellised at the various temperatures, viz., 27°C (room temperature), 86°C (on water bath), 100°C (live steam) and 102-103°C (with a small flame under the sand bath). When working at the room temperature, of course, no steam could be passed through the mixture; instead of steam, therefore, air was passed through, while the contents were being stirred up. Air was also passed through, when working at 85°C. The color of the oil was changed from yellow to brown and finally black owing to the action of the air. When working at 100°C, live steam was passed through the mixture without heating. At this temperature, a very large quantity of water was condensed (about 1.5 litres in 24 hours).

The result obtained at different temperatures are tabulated below and shown in Fig. 7.

TABLE 8—HYDROLYSIS OF COTTONSEED OIL AT DIFFERENT TEMPERATURES.

Time in hrs.	Percentage of fatty acids			
	Exp. 20 27°C	Exp. 21 85°C	Exp. 22 100°C	Exp. 2 103°C
0	1.5	1.5	1.5	1.5
4	-----	-----	59.5	55.0
7	-----	15.0	-----	-----
8	1.7	-----	76.1	70.6
11	-----	17.0	-----	-----
14	-----	-----	84.7	-----
16	-----	-----	-----	81.7
18	1.7	-----	-----	-----
24	1.75	19.9	89.1	86.6
32	-----	-----	-----	92.3
40	-----	-----	-----	93.1
44	-----	-----	-----	94.1
46	-----	-----	-----	94.6
48	-----	-----	-----	94.9
50	-----	-----	-----	95.0

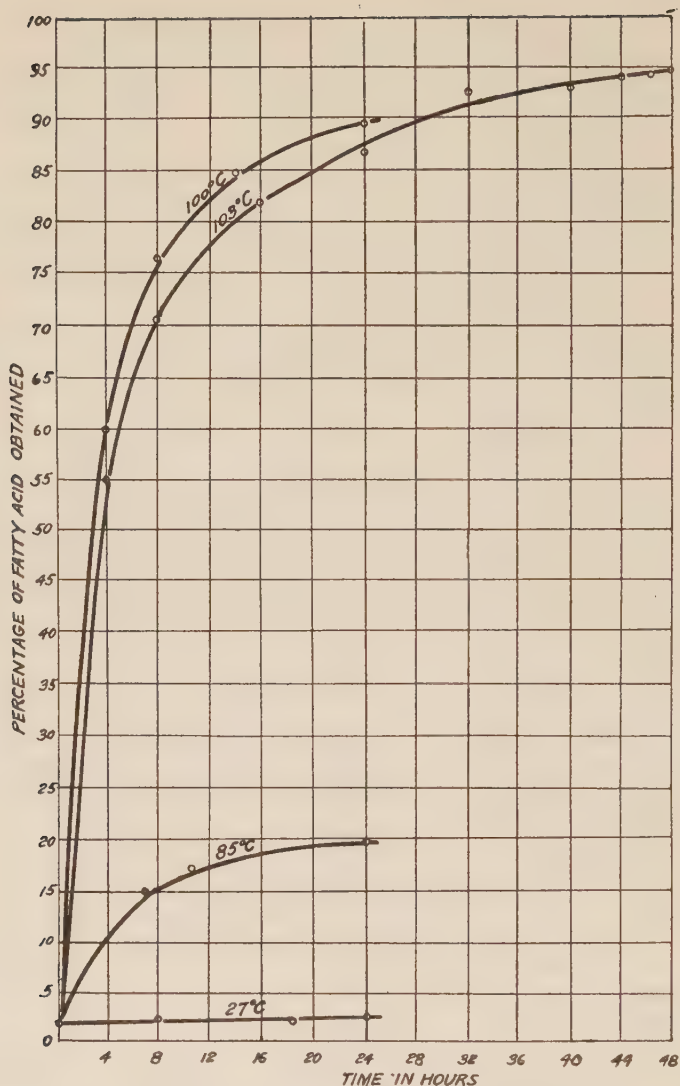


FIG 7-HYDROLYSIS OF COTTONSEED OIL AT DIFFERENT TEMPERATURES

From the above data, it will be seen that without passing steam, there is practically no change at room temperature (27°C); while at 85°C, the hydrolysis is comparatively of no practical value. At 100°C, i. e. when merely live steam is passed, the hydrolysis seems to proceed best, while with a temperature of 103°C, at which the steam is kept constantly from condensing, the hydrolysis proceeds a little less favorably. As the reverse process of esterification takes place at high temperatures and in absence of water,

a recombination of fatty acids and glycerol may take place to some extent near the final stages of decomposition. Consequently, the live steam temperature is the most favourable one in this process of hydrolysis, although the steam does condense in factory scale, where wooden tanks are used, but the quantity of water does not influence the reaction very materially.

(g) Effect of Acid Wash.—The so-called Acid Wash is an operation by which the oil or fat is first washed with a few % of 60°Be H_2SO_4 by steaming 1 or 2 hours before actually subjecting to the twitchellising operation. This treatment was said to facilitate the process of hydrolysis to some extent (Martin-Ind. Chem. Org., 5th Ed., p. 89; and Lewkowitsch-Chem. Tech. and Anal. of oils, fats and waxes, vol. 3 p. 248). The original purpose of this treatment was supposed to free the oils from all dirt, tissues or impurities present in the various fats or oils used. It might probably be thought that this is only necessary in the case of unpurified fatty materials. It will be interesting to see how this treatment would effect the hydrolysis when working with commercially purified products.

Lewkowitsch was of the opinion that an entirely neutral fat or oil requires somewhat lengthy time before the hydrolysis commences (Lewkowitsch-Chem. Tech. and Anal. of oils, fats and waxes, vol. 1 p. 86). He thought that a few % of free fatty acids seems to be necessary to induce the reaction or at least influence favorably the starting of the hydrolysis. It was thought that the treatment of Acid Wash may increase the % of fatty acids in the oil or fat so that with the free fatty acids thus produced, the hydrolysis is facilitated.

Cottonseed oil and cocoanut oil were used to study the effect of this treatment. Both oils are commercially purified product with no dirt or impurities. The oils were mixed with 2% 60°Be H_2SO_4 and steamed for 1.5 hours. The oil was then allowed to settle and was separated after 24 hours. The % of free fatty acids in the samples were determined to see whether there was any change in the % of free fatty acids before and after the treatments. Contrary to the expectation, the free fatty acid content was practically unchanged, as shown in the following table:

Percentage of fatty acids			
Cottonseed oil		Cocoanut oil	
Before	after treatment	Before	after treatment
1.47	1.47	5.1	5.0
1.48	1.50	5.1	5.4

Although this Acid Wash does not influence the free fatty acid content as expected, it, however, does facilitate the subsequent hydrolysis to a certain extent. This was clearly brought out by the experiments Nos. 2, 23, 24 and 25, though to a small extent.

In these experiments, the quantities of the reagents and the conditions were kept closely the same, except in the one case, the

oil was first washed with 2% 60°Be H₂SO₄ before subjecting to the twitchellising action, while in the other, this treatment was avoided. The charge consisted of:

100 parts cottonseed oil or cocoanut oil
 40 " water
 1 part reagent
 1 " acid

The results are shown below:

TABLE 9—HYDROLYSIS OF COTTONSEED OIL AND COCOANUT OIL WITH AND WITHOUT ACID WASH.

Time in hrs.	Percentage of fatty acids			
	Cottonseed oil		cocoanut oil	
	Exp. 2	Exp. 23	Exp. 24	Exp. 25
	with	without	with	without
	Acid wash	Acid wash	Acid wash	Acid wash
0	1.5	1.48	5.2	5.1
4	55.0	54.2	57.0	55.2
8	70.5	68.3	80.1	76.7
12	-----	-----	86.0	85.3
16	81.7	79.5	-----	-----
17	-----	-----	88.5	87.3
24	86.6	85.8		
32	92.3	91.9		
40	93.1	93.0		
44	94.1	-----		
48	94.9	94.9		
50	95.0	-----		

From these experiments, it will be seen that not only the Acid Wash removes the dirt and impurities from the crude oil but also facilitate hydrolysis even with commercially purified oils, though to a very slight extent. Cocoanut oil was especially studied because present opinions differ as to the advantages of so treating this oil (Directions for using "Liquid Kontakt Saponifier"). It should be noted that the cocoanut oil used was a commercially purified product, of a syrup consistency, a clear yellow color and has an acid value of 5.1, a saponification value of 245.2 and a R. M. value of 8.3. The % of fatty acids obtained was therefore that of the insoluble fatty acids which amounted to the above determined value on account of the volatile fatty acids which were volatilised in this process. In light of these experiments, the Acid Wash seems, therefore, to facilitate the hydrolysis in some way, though to a slight extent.

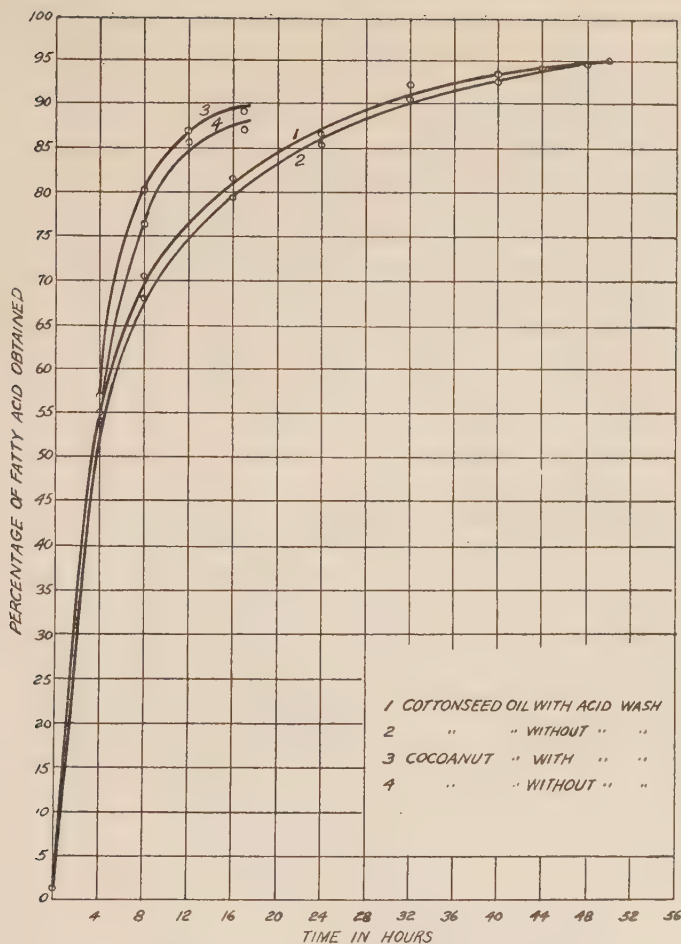


FIG. 8-HYDROLYSIS OF COTTONSEED OIL AND
COCOANUT OIL WITH AND WITHOUT ACID WASH

VI INFLUENCE OF FOREIGN SUBSTANCES.

The discovery of the new catalytic processes and of suitable catalysts has necessarily been made by the purely empirical method of trial and observation, except in so far as the choice for a probable catalyst was guided by analogy with known reactions. And the same is true regarding the study of catalytic "Promoters" or "Accelerators" and catalyst "Poisons," which, from an industrial standpoint are almost of equal importance to that of the catalyst itself.

Although the systematic and intensified development of catalysis in the future should depend upon a better understanding of the theoretical principles which underlie the mechanism of the various types of the catalytic processes, the chemists in search of the industrial catalysts, still proceed by a method of trial and purely experimental study and many catalysts have been thus discovered.

In view of these facts, some metal and neutral salts which had been found to give an accelerating effect on similar reactions were tried with a view to find some "*Promoters*" or "*activators*" as they were called, by which Twitchell's process of hydrolysis might be further accelerated. Thus zinc dust and copper sulphate were found by Lewkowitsch to accelerate somewhat the hydrolysis of lard by HCl of Sp. Gr. 1.16 (Lewkowitsch-Chem. Tech. and Anal. of oils, fats and waxes, vol. 1, p. 82) and manganese sulphate by Nicloux to activate the hydrolysis of oils and fats by ferments (Loc cit, p. 92). Here zinc dust, ammonium sulphate, copper sulphate and manganese sulphate were tried and none of them was found to exert an activating effect, but instead, they all exercised an inhibiting influence to a more or less extent.

In these experiments, the charge consisted of:

100 parts cottonseed oil
 40 " water
 1 part reagent
 1 " acid

and the respective substances indicated in the table. The experimental conditions were carefully kept the same as in other experiments with the foreign substances added at the beginning, with the exception of MnSO_4 which was added after 8 hours, as it was thought that after the hydrolysis had proceeded to a certain extent, the addition of it may have a more profound effect.

From a theoretical point of view, any substance that will retard a reaction should be considered of equal importance as the ones which accelerate; the results are therefore given below:

TABLE 10—HYDROLYSIS OF COTTONSEED OIL WITH TWITCHELL REAGENT IN PRESENCE OF FOREIGN SUBSTANCES

Time in hrs.	Percentage of fatty acids			
	Exp. 26 1% $(\text{NH}_4)_2\text{SO}_4$	Exp. 27 1% CuSO_4	Exp. 28 0.2% MnSO_4	Exp. 29 1% Zn dust
0	1.5	1.5	1.5	1.5
4	17.4	31.2	32.1	19.7
8	42.0		65.1	23.0
10				
12		65.8	77.9	
14	50.9			26.4
16		75.4	82.3	26.2
20	60.3			
24	65.5	80.2	83.4	29.3
28	72.5			29.5
32	75.1	86.2	88.3	
35	78.8			
36				35.6
40	78.2			37.5
44	80.5			
48		87.1	88.4	41.1
54.5				46.0

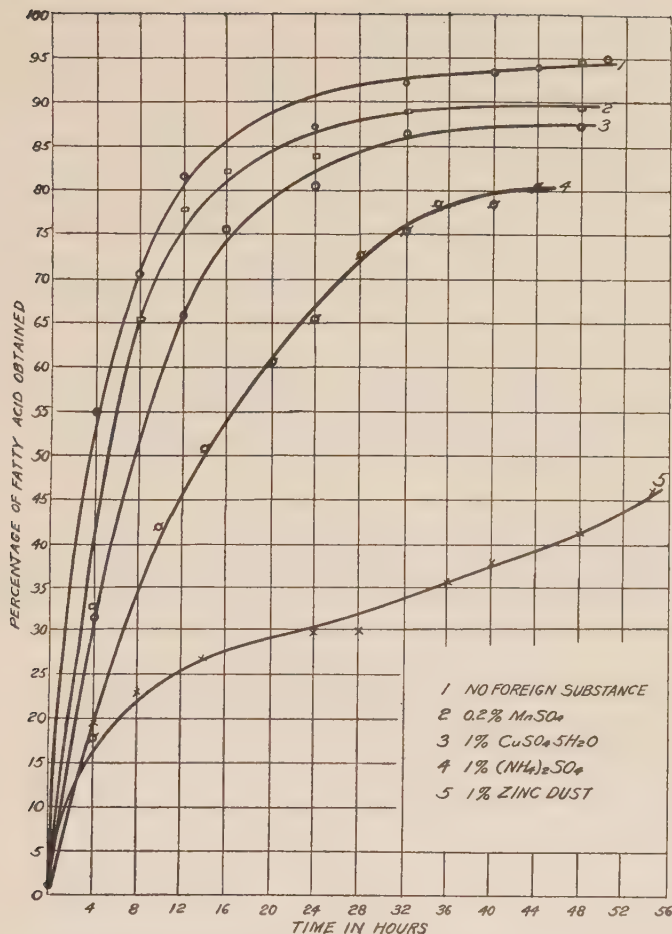


FIG. 9-HYDROLYSIS OF COTTONSEED OIL IN PRESENCE OF FOREIGN SUBSTANCES

Poma has shown that in acid catalysis of ester hydrolysis, the influence of the neutral salts on the velocity of the reaction depends in high degree on the nature of the anion. Further, the influence of the salts differs in degree with the anion employed; and the accelerating action diminishes with diminishing degree of dissociation as calculated by conductivity method and finally becomes with weak acids, not an acceleration, but an retardation. (Redeal and Taylor-catalysis in Theory and Practice, 1918 Ed., p. 255).

Therefore in the above experiments, a few of the salts of H_2SO_4 were chosen for the reason that H_2SO_4 should rank among the strong acids. In spite of what we should expect from the above consideration, the influence of all the sulphates here studied is to retard the hydrolysis.

In dealing with the catalysis by acid, the activity has been shown to be proportional to the concentration of the H-ions. According to the dissociation theory, addition of a neutral salt depresses the degree of dissociation of the acid and therefore the H-ion concentration in accordance with the law of mass action. This was shown to be true by Arrhenius in the case of weak acids. With strong acids, however, the influence of the neutral salts is by no means so readily explicable (Zeits. Phys. Chem., 1894, p. 492). The addition of KCl accelerates the catalytic activity of HCl in ester hydrosis, whereas on the dissociation theory, a diminution of the reaction velocity would be expected. This has been explained by assuming the non-ionised portion of the molecules to be more active catalytically. This would not apply to the present cases, since retardation took place.

Also Arrhenius' theory, that the increase of the ionic concentrations displaces the equilibrium between the active and inactive forms of the substrate in the direction of increase of active modification, would not apply, since then, an acceleration should be expected.

To the present cases, the results shown by H. Trey might be applicable (Journ. Prakt. Chem., Vol. 34, 1886; p. 353). He showed that the reaction velocity of HCl on ester hydrolysis was accelerated by presence of its salts, but that of H_2SO_4 was retarded by the presence of its salts.

The retardation of ester hydrolysis by the presence of foreign substances in general has been explained by assuming that, the degree of ionisation of the ester or the catalyser is diminished, or else, the ester or the catalyser combines with the foreign substance, thus diminishing the active mass of the ester or the quantity of the available catalytic agent (Mellor-Chem. Statics and Dynamics, 1904 Ed., p. 285; Zeits, Phys. Chem. 1901, p. 612).

This assumption is the most plausible one that can be advantageously applied to the present case, when we consider the fact, that in all these cases, the mixture became viscous with evolution of gases. Some reaction or combination might have taken place between the catalyst and the foreign substances added. The most apparent retardation was shown in the case of zinc dust, which might react with H_2SO_4 or the Twitchell reagent, thus diminishing the activities of them and retardation taking place.

Moreover, the experiments of ester hydrolysis made by Kellog showed that the relation between the concentration of the salt, on the one hand, and the acceleration produced thereby, on the other hand, is by no means a simple one; the effect, in the case of KCl, passing through a maximum somewhat between 1% and 20% and changing sign somewhat between 20% and saturation. (Journ. Am. Chem. Soc., 1909, p. 403). Similar relation might also exist in the case of acid catalysis of ester hydrolysis, and the retardation in the present cases might be due to a question of concentration. Therefore, the small number of experiments made along this line does not, however, permit general conclusions to be drawn.

The interesting phenomenon of neutral salt action has occupied the attention of a considerable number of investigators and as yet it is impossible to state, in what direction the theory will develop, or how far it will generalize the various factors observed in such reactions.

VII—INFLUENCE OF THE PRODUCTS OF REACTION

In some reactions, substances are produced which themselves have a positive or negative effect on the speed of the change; this phenomenon is known as "Auto-catalysis," positive or negative as the case may be. Thus, e. g. the hydrolysis of esters by water is generally accelerated by the addition of acids, and it has been observed that the acid produced by the hydrolysis of the ester itself acts catalytically; hence it is easy to understand why it is that, the action of water on an ester proceeds slowly at first and rapidly increases in velocity as the acid accumulates in the system. Numerable instances, in which certain substances produced in the system have an inhibiting effect on the progress of the change, are also known.

This is an exceedingly important phase, concerning the study of the rate of a reaction, as here not only the influence of the mass action, in the case of a reversible reaction, may come in, but also some other effects on a special type of reaction, have to be taken into account. Thus in the case of ester hydrolysis just cited, the free acids formed accelerates the progress of the reaction, whereas the hydrolysis of the glycerides by ferment is inhibited by the presence of free acids (Lewkowitsch-Chem. Tech and Anal. of Oils, Fats and Waxes, Vol. 1, 1913 Ed., p. 93).

A series of experiments was instituted to see what influence the products of reaction, viz., fatty acids and glycerine, would have on the progress of the reaction by Twitchell Process. In carrying out these experiments, the charge consisted of:

	100 parts	cottonseed oil
	40 parts	water
	1 part	reagent
	1 part	acid
	5 parts	fatty acids
or 20	" "	" "
or 5	"	glycerine
or 20	"	"
or 20	"	both

and was twitchellised as usual. The results and the accompanying curves were shown below:

TABLE 11—HYDROLYSIS OF COTTONSEED OIL IN PRESENCE OF THE PRODUCTS OF REACTION

Time in hrs.	Percentage of fatty acids					
	Exp. 2	Exp. 30	Exp. 31	Exp. 32	Exp. 33	Exp. 34
	No glycerine or fatty acids added	5 gms glycerine	5 gms fatty acids	20 gms glycerine	20 gms fatty acids	20 gms glycerine and fatty acids
0	1.5	1.5	5.0	1.5	23.0	23.0
4	55.0	51.3	55.8	4.3	63.8	45.4
8	70.6	72.4	80.0	39.7	77.6	64.4
12	-----	-----	91.2	-----	-----	-----
16	81.7	87.9	93.3	69.0	91.4	78.5
20	-----	-----	93.7	-----	-----	-----
24	86.6	92.9	94.9	79.3	92.7	84.6
32	92.4	-----	-----	83.2	97.0	87.1
36	-----	92.9	-----	-----	-----	-----
40	93.1	92.5	-----	83.1	96.5	89.4
44	94.1	91.9	-----	82.7	-----	-----
48	94.9	-----	-----	82.1	97.4	88.8
50	95.0	90.9	-----	-----	-----	-----

From an examination of the results and especially the curves in Fig. 10, it will be noted that the addition of 5 gms of glycerine even accelerates the reaction at the start, but a reversible reaction takes place near the end of the reaction, whereas with the addition of 20 gms. of glycerine, the rate is much slower. This phenomenon is most probably due to the mass action effect of the reversible reaction; as with only the glycerine produced in the reaction and with no glycerine added at the beginning, the equilibrium seems to take place when about 95% of the neutral oil has been hydrolysed, whereas, in the presence of 5 gms. and 20 gms. of glycerine added, the reversible reaction takes place at an earlier stage.

In describing Twitchell's process, Lewkowitsch stated that in the presence of a large excess of glycerine, the process is a reversible one, triglycerides being formed from free fatty acids and glycerine (Lewkowitsch-Chem. Tech and Anal. of Oils, Fats and Waxes, Vol. 1, p. 248). This may be advantageously applied to explain the usual operation of removing the aqueous glycerine water and replacing with fresh water after the so-called "First boil" when about 85% to 90% of the fatty material has been hydrolysed.

The influence of the addition of a few percent of fatty acids however, is very remarkable. It shows, on the one hand, that at the beginning, the rate of hydrolysis is practically the same with or without the presence of fatty acids i. e. in the case of an oil containing a few percent of fatty acids or in the case of a practically neutral oil. This does not agree with the ordinary assumption that the presence of fatty acids seems to be essential in initiating the hydrolysis and with a perfectly neutral oil or fat, the starting of the hydrolysis takes a somewhat lengthy time (loc cit). On the

other hand, its accelerating effect after a certain period of time e. g. from 5th or 6th hour up, is exceedingly noticeable. Thus it took about 28 hours to obtain 37% of fatty acids from 55% to 92.3% without the presence of fatty acids at the beginning; whereas it took only 8 hours to obtain 36% from 55.8% to 91.2% when 5 gms. of free fatty acids were added at the start. This portion of the hydrolysis is the most difficult, and the rate, the slowest, in ordinary cases, thus prolonging the requisite time for the practical completion to an inconvenient length.

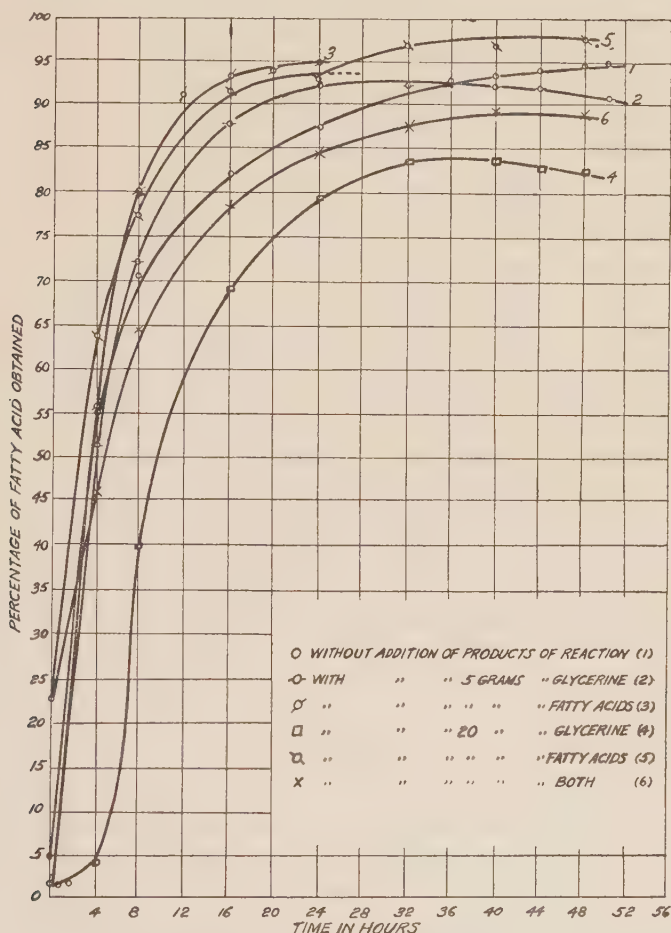


FIG.10—HYDROLYSIS OF COTTONSEED OIL IN PRESENCE OF PRODUCTS OF REACTION

It is largely due to the accelerating effect of the fatty acids in this case that the time of hydrolysis can be shortened to about 50%.

The acceleration is approximately the same in presence of 20 gms. of fatty acids as in presence of 5 gms.; in the latter case, the effect is even more evident.

From the above considerations, the general conclusion is that glycerine has an inhibiting effect on the progress of the hydrolysis due to the reversed recombination; while fatty acids, on the other hand, have an accelerating effect. These facts are more clearly brought out by the curves, 3, 5, and 2, 4 in comparison with curve 1. Experiment 34 with 20 gms. of both glycerine and fatty acids shows that the inhibiting effect of glycerine is more than counter-balanced by the accelerating effect of the fatty acids present and therefore curve 6 is located between curves 4 and 1.

Moreover, it is interesting to call attention to the fact that, in the hydrolysis of an ester, like ethyl acetate, by water, the reaction proceeds slowly at first and rapidly increases in velocity as the acids accumulate in the system, whereas in this case, the hydrolysis proceeds fastly at first even without the presence of fatty acids and slows down as fatty acids accumulate.

While the velocity falls off as the fatty acids accumulate, the addition of free fatty acids at the start again produces a remarkable acceleration after a certain period. It seems, therefore, to be evident, that each special type of hydrolysis should be separately considered. This phenomenon can hardly be explained by the earlier emulsification that was observed to take place, since at the beginning, the percentage of hydrolysis came to about the same within the experimental error, with or without the presence of fatty acids. A probable assumption would be, that the rate of the reaction is at its full speed at the beginning, since the molecules of the oil are all in the triglyceride condition whose rate of hydrolysis is in the ratio of 3:2:1 against that of di- and mono-glycerides (Journ. Prakt. Chem. 1897, p. 417; Zeits. Phys. Chem., 1906, p. 558; Zeits. Elect. Chem., 1907, p. 307), so that whether there is a better emulsification or not, does not apparently influence the speed of the reaction. But as the rate of the reaction falls off gradually on account of the formation of di- and mono-glycerides, this effect of better emulsification produced by the presence of fatty acids begins to become appreciable.

VIII—IMPROVEMENT OF THE REAGENT AND THE PROCESS

During the preliminary study of the "Liquid Kontakt Saponifier," it was pointed out, that this reagent dissolves only partly in absolute alcohol, leaving a dark, grey, viscous residue. Apparently this reagent consists of two parts, one soluble and the other insoluble in absolute alcohol. These two parts may both be active in their hydrolysing activity or one must be co-operated with the presence of the other, so that the splitting action can be effected. Or else, one of the two parts is only active in hydrolysing power, and the other is just present as an impurity or an inert constituent.

This can easily be found by testing the activity of the same amount of the different parts as obtained by actually making hydrolysing experiments. Accordingly, these experiments were carried out as usual, using 1% of the alcohol-soluble part in one case, and 1% of the alcohol-insoluble part in another.

The results were recorded below in comparison with the same amount of the original reagent:

TABLE 12—HYDROLYSIS OF COTTONSEED OIL WITH
THE IMPROVED REAGENT

Time in hrs.	Percentage of fatty acids		
	Exp. 2 1% original	Exp. 35 1% alcohol soluble part	Exp. 36 1% alcohol insoluble part
0	1.5	1.5	1.5
4	55.0	59.0	
7		80.0	
8	70.6		1.6
9		83.9	
11		91.2	
14		93.0	
16	81.7		1.6
17		94.8	
24	86.6		
32	92.1		2.5
40	93.2		
44	94.1		
48	94.9		2.5

In the above table, experiment 2 shows the rate of hydrolysis by using 1% of the original "Liquid Kontakt Saponifier," experiment 35, that by using 1% of the alcohol soluble part and experiment 36, that by using 1% of the alcohol insoluble part. In experiment 35, the mixture was well emulsified at an earlier stage than in experiment 2; whereas in experiment 36, the mixture was never emulsified and the hydrolysis did not seem to proceed after a long time. This is clearly shown in Fig. 11.

By the purification and concentration of the original reagent mentioned above, it is rendered much more effective in hydrolysing power, which amounts to about three times, as was shown in experiment 35, thus only requiring one-third of the time demanded by the original reagent.

The actual composition of the reagent as applied to the licensees under the name of "Liquid Kontakt Saponifier" is not exactly known or is kept secret as a consequence of trade policy. The writer, therefore, does not feel justified in making detailed statements as to the conditions in which it is prepared besides pointing out that it is understood to be made from mineral oil sludge.

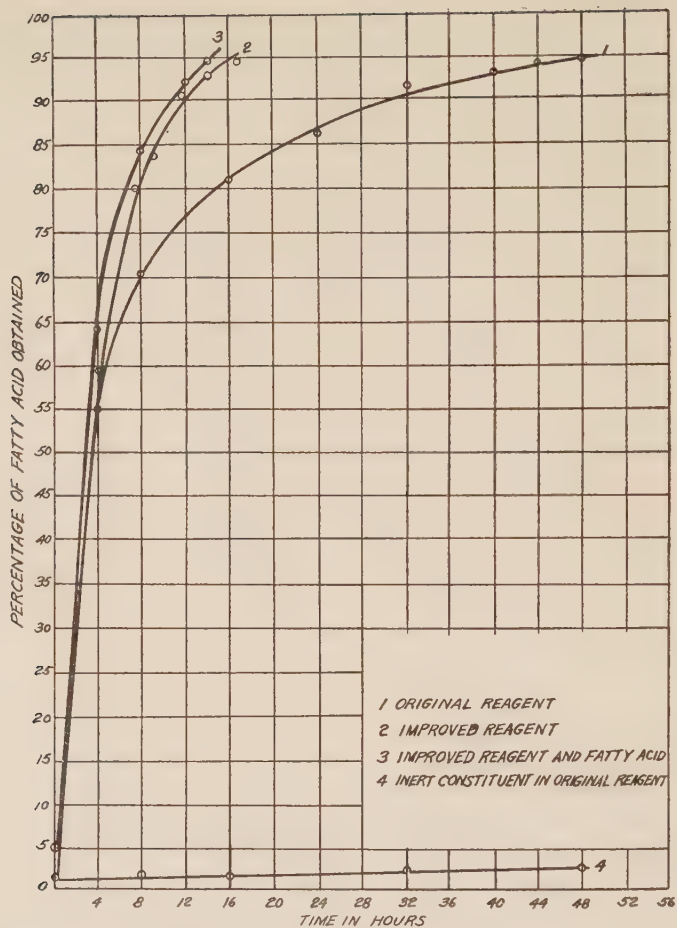


FIG. 11-HYDROLYSIS OF COTTONSEED OIL WITH IMPROVED REAGENT AND IN PRESENCE OF FATTY ACID

A few experiments were instituted to make sulphonic acids from mineral oil sludge according to the processes given in the U. S. Patents (U. S. P. 1,303,779, 1,319,027 and 1,330,624). Sludges from Standard Oil Co. and The Pure Oil Co., Heath, O., were investigated.

To 100 parts of sludge were added 150 parts of water and the mixture was let stand over night. Much heat was generated and SO_2 evolved when water was added. After standing, the dark oil floating on the top was separated from the water solution which had a clear purple red color when viewed from a test tube. To this solution, was added lime until it gave an alkaline reaction to litmus. The precipitated CaSO_4 was filtered and a neutral solution having a light wine color was obtained. To the neutral solution was added

sufficient CaCl_2 until no more dissolved. This salted out a light yellow colored, plastic, sticky compound which is very soluble in water. With age, the color became darker than when freshly prepared. The compound was dissolved in water and treated with H_2SO_4 to liberate the free sulphonic acids. This was treated with absolute alcohol which solution was then evaporated, leaving a dark yellowish, viscous substance. It had a high emulsifying power, forming emulsion when its water solution was shaken. 1% of this reagent was tested for its hydrolysing property by twitchellising as usual, the following results showed it to be very effective.

Exp. 37	
Time in hrs.	% fatty acids
4	56.2
8	80.1
16	88.5
20	93.4
24	94.6

As to the operations concerning the carrying out of the process, Reuter worked more on the mechanical side than on the chemical side (U. S. P. 1,068,079; 1,219,485; 1,227,198). He improved the mechanical devices so that any volatile compounds obtained in the hydrolysis could be easily recovered. He preferred a successive treatment by using a smaller amount of the reagent and acid at a time and making 3 boils of 24 hours each instead of 2 boils, after each of which the aqueous glycerine layer was separated and fresh water together with more reagent and acid was added. Moreover, he bleached the fatty acids with decrolin by which it was claimed, that the fatty acids obtained were better colored. This successive treatment was found in the previous pages to give a much better color of the fatty acids but it took a much longer time.

According to the Twitchell Process, the fatty material is acid washed by passing steam through it in the presence of 1 or 2% of 60°Be H_2SO_4 . The purified fat is then mixed with about 40% or 50% of water together with the necessary amounts of reagent and acid and twitchellised. As mentioned above, 2 boils of 24 hours each are usually given; after the first boil, the aqueous layer of glycerine is separated and fresh water amounting to about 15% is added, together with about 0.25% acid. This is done principally for the reason, that the speed of hydrolysis slows down after that time, when about more than 85% of the oil is hydrolysed. The addition of a little more acid accelerates the reaction which takes another 24 hours for approximate completion.

It was found not necessary to use Acid Wash and make 2 boils by the improvement of the reagent which is so much more active that the usual slowing down of the rate of the reaction is not so apparent as distinctly shown by the curves in Fig. 11. Even in the case of difficulty saponifiable cottonseed oil, approximate complete hydrolysis can be obtained in about 17 hours. With 1%

of the improved reagent, the time necessary can further be shortened to about 14 hours in hydrolysis of cottonseed oil by adding 5% of the free fatty acids at the beginning of the operation. The data follows:

Saponification of cottonseed oil	
1% improved reagent, 5% fatty acids, 1% acid and 40% water	
Time in hrs.	% fatty acids
0	5.0
4	64.1
8	84.4
12	92.2
14	94.8

The accelerating effect is clearly shown in curve 3, Fig. 11. So in general, the hydrolysis can be completed in one boil. The process may therefore be modified by using 1% of the reagent with the equivalent amount of the 60°Be H_2SO_4 together with about 40% of water by passing steam at 100°C through the mixture which is constantly agitated. The time for the completion of the reaction varies with the different oils or fats in from 8 to 18 hours in the case of the difficulty saponifiable oils. As by the improved reagent, the speed of the reaction was not so sluggish after about 85% oil was hydrolysed, the separation of the aqueous glycerine layer and the changing of the fresh water with the addition of a small amount of acid were considered not necessary. Using the improved reagent and the process, from two-thirds to one-half of the time required originally can be saved, i. e., a plant of the same capacity can do as much as three times the work.

If time is a serious question, free fatty acids may be added at the beginning together with the improved reagent. The time necessary will thus be further reduced as shown before.

Besides the shortening of the time, this improvement of accelerating the hydrolysis should have more advantages than those by activating with organic or inorganic salts. It is easily seen that this improvement of the reagent and the process introduces no undesirable impurities into the products obtained, neither into the fatty acids nor into the glycerine layer; whereas an acceleration by other organic or inorganic salts introduces the impurities more or less undesirable. By this modification of the reagent, not only no impurities are introduced but also the inert constituents in the original reagent are removed. This cannot do any harm to the system besides increasing the efficiency of splitting.

Furthermore, the treatment of the original reagent with alcohol does not necessitate much expense, as the alcohol can be completely recovered by simple distillation and can be used over and over again. The addition of a few percent of free fatty acids at the beginning, if necessary, also does not increase any more cost, as fatty acid is one of the products of reaction in a splitting plant. The addition of free fatty acids again introduces no foreign im-

purities to the system, as it is one of the products produced in the system. The color of the fatty acids obtained was found to be even lighter colored than with original reagent on account of the time thus shortened.

From the above consideration, this improvement of the reagent and the process has not any disadvantage, and should be of very great practical value to a splitting plant, as with the same space, three times as much work can be done in a certain period of time, and yet no undesirable impurities or treatments necessitated by this change are introduced. As the time is shortened, the condensation of water will, of course, be less, a more concentrated glycerine solution than what could be produced, can be obtained, thus saving the time and cost of evaporating and concentrating the sweet water. It is hoped that more work will be done along this line, so that catalysts will be found, by which the hydrolysis of the insoluble triglycerides, which takes a long time, could be effected as in the case of lower soluble glycerides which can be effected in very short period.

IX—STUDY OF THE REAGENTS ON THE HYDROLYSIS OF DIFFERENT OILS AND FATS

Lowenherz has shown that the influence of the alcohol radical of the ester on the rate of hydrolysis is slight, but that the velocity is to a marked degree dependent on the nature of the ester acid (Zeits, Phy. Chem., 1894, p. 389). The velocity of hydrolysis becomes increasingly slower with increasing complexity of acid. As different oils or fats have different compositions, they naturally would behave differently when subjected to hydrolysis by the Twitchell Process. Since the factors effecting the process of hydrolysis by this method have been studied somewhat in detail with cottonseed oil, it was thought desirable to study a few more oils and fats to see how the different oils and fats behave and to give an index of how the manipulations should be varied for the individual oil or fat, although no effort was made to study every oil or fat in detail as to the various factors. Again, it is the purpose to make a comparative study of the activity of the original and the improved reagent on the hydrolysis of the different oils and fats. According to the ease with which the different oils or fats behave, the manipulation and the length of time to which the treatment of the oils or fats has to be continued, can be suitably varied.

Besides the cottonseed oil which has been studied somewhat in detail with both reagents in the previous pages, the remaining oils and fats have been treated similarly as follows:

The charge consisting of:

- 100 parts of the respective oil or fat
- 40 parts water
- 1 part original or improved reagent
- 1 part acid

was twitchellised as usual. In the case of original reagent, two boils were given for those difficultly saponifiable oils and fats;

after the first boil of 24 hours, 0.25% acid was added and a second boil was given; whereas in the case of improved reagent, 1 boil of from 12 to 21 hours was continued.

The sesame oil used was a commercially purified product, having a clear, yellow color. It had a saponification value of 188.6 and an acid value of 1.02 according to the method in Leach's food analysis, The soy bean oil had a saponification value of 193.3 and an acid value of 5.8. It seemed to be not a purified product, as it had a dirty brown color with a peculiar smell. The tallow was mutton tallow of a saponification value, 193.3 and an acid value, 3.5. It is a slightly yellowish white solid. The constants of the cocoanut oil used were given before.

The results of the experiments are tabulated below and shown in Fig. 12, 12A and 12B.

TABLE 13—HYDROLYSIS OF DIFFERENT OILS AND FATS
WITH 1% OF THE ORIGINAL OR IMPROVED
REAGENT

hrs.	Percentage of fatty acids-									
	Tallow		sesame oil		soy bean		cocoanut		cottonseed	
	Exp. 38	Exp. 39	Exp. 40	Exp. 41	Exp. 42	Exp. 43	Exp. 24	Exp. 44	Exp. 2	Exp. 35
4	70.3	77.4	75.8	78.9	10.7	35.1	57.0	63.5	55.0	59.5
7										80.0
8	87.6	88.2	86.1	89.3	13.8	68.2	80.1	81.8	70.6	
9										83.9
11										91.2
12		94.7		93.4			86.0	88.6		
14										93.0
16	91.2		90.9	94.2	63.1	90.7			81.7	
17							88.5			94.8
20	94.8			95.6						
21						94.4				
24			93.9		79.3				86.6	
32			94.3		83.0				92.1	
40					88.2				93.2	
44									94.1	
48					94.4				94.9	

From the above table, it will be seen that, of all the oils and fats studied, soy bean oil and cottonseed oil might be considered as the type of the difficulty saponifiable ones and tallow as the one most easily saponified. A glance of the above data will show that the different oils and fats behave quite differently in the process of hydrolysis. It should be noted, that with the same oil or fat, the time taken to hydrolyse the same amount of the fatty material to about the same extent is much shorter, using the same amount of the improved reagent; in general from one-third to one-half of the time only being necessary.

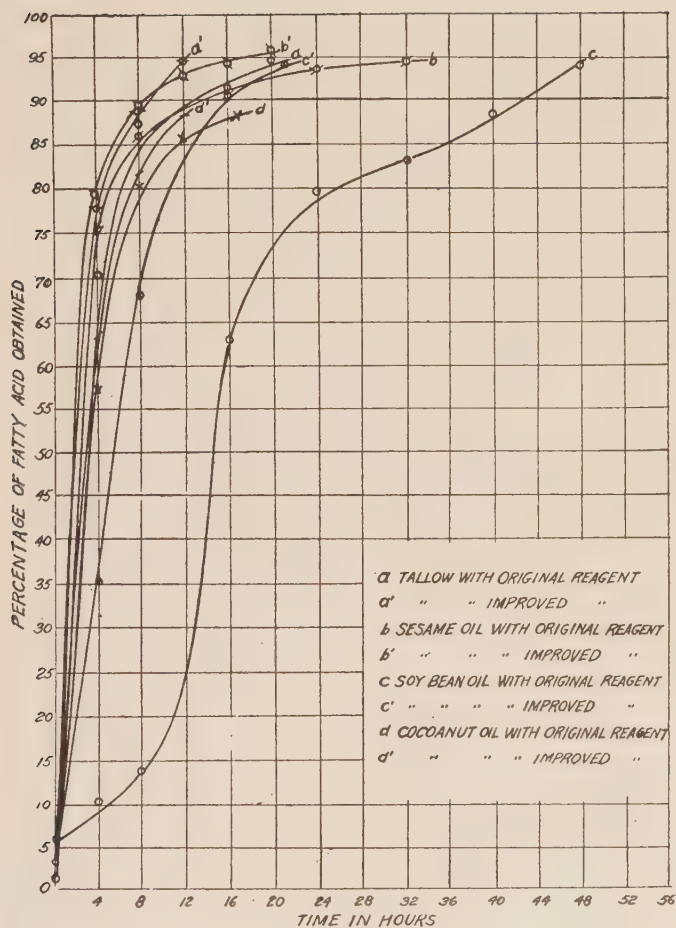
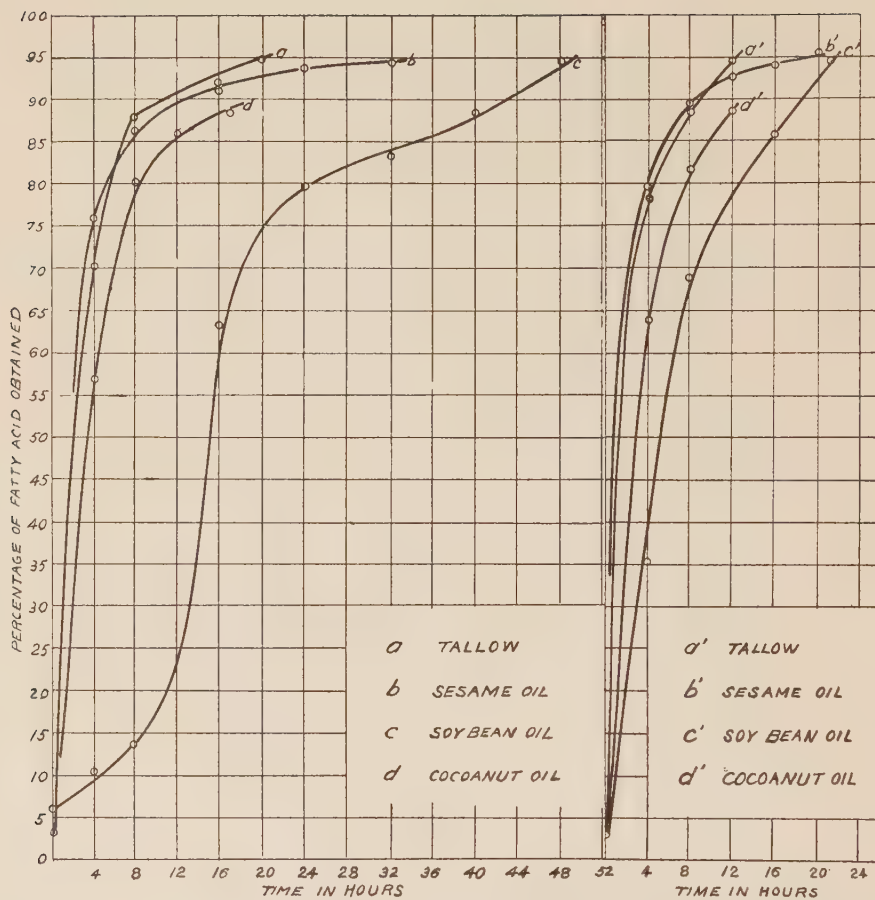


FIG.12-COMPARISON OF ORIGINAL AND IMPROVED REAGENT



X—THE COURSE OF THE REACTION AND THE MECHANISM OF THE ACTION OF “LIQUID KONTAKT SAPONIFIER”

The use of the catalytic reagent discovered by Twitchell in chemical reactions involving the splitting of the higher glycerides on the one hand (U. S. P. 601, 603; 1,330,624), and their synthesis from free fatty acids and glycerine on the other (U. S. P. 844,426), has, of recent years, been the subject of technical application. Although its stability for such reactions was first established by Twitchell in 1900 and some investigations dealing with it have since been published, none of these, so far as I am aware, deals with the subject from the dynamic standpoint; and of course, both from the manufacturing and theoretical point of view, the velocity of a reaction is a very important consideration.

As mentioned above, the main object of this investigation was not to study the mechanism of the reaction nor to find out the order of the reaction which could form a separate topic; nevertheless, some of the data obtained would serve a preliminary study for this purpose, and they are discussed here.

The oil chosen for this study was purified cottonseed oil and the catalyst was the “Liquid Kontakt Saponifier” placed on the market by the Twitchell Process Co. The process was carried out as afore described and the progress of the reaction was followed by the method given above. The results obtained at a temperature of about 102-103°C were recorded below:

Time in hrs.	x	a-x	$k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$;
0	0	100.0	
2	13.4	86.6	0.03124
5	43.4	56.6	0.04943?
7	51.2	48.8	0.03220
11	71.1	28.9	0.04900?
13	76.5	23.5	0.04443
16	79.8	20.2	0.03111
20	83.4	16.6	0.03551
24	86.5	13.5	0.03282
29	90.1	9.98	0.03133
34	93.9	6.1	0.03344
38	94.1	5.85	0.03244

In the above table, x = the percentage of free fatty acids obtained and a-x = the percentage of the unhydrolysed oil at the time indicated in the first column. As the reaction of the first order is independent of the unit by which the concentration is expressed, a=100 gms of oil may be taken as the initial concentra-

tion. k gives the velocity constant calculated from the formula of the mono-molecular reaction, $k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$. (Mellor-Chem. Statics and Dynamics, 1904, p. 31).

From the above table, it is evident that the rate, at which the reaction proceed, falls off as less and less oil remains. In the first 5 hours, the change of oil into fatty acids is 43.4%; in the 5 hours from 24th to 29th, the change is only 3.6%. This is in accordance with the principle of Guldberg and Waage that the amount transformed in a given time will fall off as less oil remains to undergo decomposition.

The chemical equation expressing the reaction may be represented as



As the reaction progresses, water disappears as well as oil; but if we consider, that the reaction takes place in presence of a large quantity of water, the change in the active mass of water can only be very slight, and the concentration of water may be taken as constant in calculation.

Although the hydrolysis of oils and fats is in reality a reversible reaction, but in the presence of a large amount of water (Journ. Am. Chem. Soc., 1907, p. 566), and not at a high temperature and pressure, the decomposition is practically complete, and the reaction is of the same type as the acid hydrolysis of esters and the inversion of cane sugar.

From the values, k , of the expression $\frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$ as given

in the fourth column of the table, it will be seen that they remain constant throughout the reaction with 2 or 3 exceptions. The numbers can be considered sensibly constant within the limits of the experimental error, if the various disturbances resulting from the difference in conditions due to the long time the process has to be continued and the difficulty of following the reaction in a heterogenous system, have taken into consideration. Moreover, it is very difficult to keep up a thorough inter-mixing of fat and acidulated water under the conditions of the experiments.

Geitel showed in the case of soluble triglycerides, that the hydrolysis was apparently a mono-molecular reaction and that the velocities of hydrolysis of mono., di- and tri-acetate in dilute acids were in the ratios of 1: 2: 3 (Journ. Prakt. Chem., 1897, p. 417; Ibid., 1898, p. 113). Abel (Zeits, Phys. Chem., 1906, p. 558) and Kremann (Zeits. Elect. Chem., 1907, p. 307) further showed that the apparent mono-molecular nature of the hydrolysis of the gly-

cerides was a mathematical consequence of the fact that hydrolysis occurred in the three successive stages, the rates of which were in the ratio of 3: 2: 1.

From these considerations, it is easy to see that the course of the reaction is of the first order and why the oil was hydrolysed at a much greater rate at the beginning when the oil was in the triglyceride condition, and with much less speed when a great part of the triglycerides was changed into the di- and mono-glycerides.

More evidence is furnished when we consider the phenomenon, that, part of the reagent is precipitated in the presence of more than four times its quantity of acid and can be filtered out, although its physical condition was somewhat changed. Attempts to recover all of the reagent did not succeed.

Further indications as to the action being catalytic in nature are to be found in using a very small amount of the reagent and in its capability of synthesising glycerides from fatty acids and glycerine as well as accelerating hydrolysis.

Twitchell gave a method of estimating glycerine or fatty acids by effecting synthesis with either excess of fatty acids or glycerine with his naphthalene-stearo-sulphonic acid reagent (Journ. Am. Chem. Soc., 1907, p. 566). The same experiment made with the "Liquid Kontakt Saponifier" under slight modifications showed the following results:

ESTERIFICATION OF GLYCEROL

Exp. No.	% of combined glycerol found (Original sample contains 67.6% glycerol)
45	15.7
46	31.4
47	66.9

In these experiments, 1gm glycerine of commerce of Sp. Gr. 1.1768, which contained 67.6% glycerol by acetin method, was diluted to 100 cc; 5 cc of which is equivalent to 0.05 gms of the original sample. For fatty acids, commercial stearic acid purified by boiling with dil. HCl and drying, was used. For the experiments, 5 cc of the glycerine solution, 1 gm of the stearic acid and 2 cc of the 10% solution of the reagent were heated in a 120 cc round bottom flask on a boiling water bath. The water evaporated in about an hour and the heating was continued another 4 hours. After that time, enough alkali solution to neutralize the acidity of the reagent determined beforehand was added and then 50 cc of neutralized alcohol. The mixture was warmed to dissolve all the uncombined fatty acids and then titrated with standard alkali solution in presence of phenolphthalein as indicator. Experiments with the same amount of the other constituents but without the presence of glycerine were made side by side and titrated in the same way. In exp. 45, no mineral acid was present. In exp. 46, a definite amount of sulphuric acid was added, also to the blank, and the combined glycerol was found to be 31.4%. In the above experiments 45 and 46, alkali solution and alcohol were added when the solution was still warm. In exp. 47, the mixture was first cooled and then alkali solution and alcohol were added and warmed again just enough to dissolve the uncombined stearic acid before titrating. The combined glycerol was found to be 66.9%. In the last experiment, 47, the mixture required 17.0 cc of KOH to neutralize the uncombined fatty acids, whereas the one with no glycerine present required 22.1 cc of the same solution. The difference of 5.1 cc represents the amount of glycerine combined with the stearic acid. 1 cc of the standard KOH equivalent to 0.00656 gms

0.00656x5.1x100
=66.9.

glycerol and the percentage of glycerol found was 0.05

Thus under suitable conditions, "Liquid Kontakt Saponifier" is able to effect synthesis as well as hydrolysis much in the same manner as platinum black is capable of acting as an accelerator both in hydrolysing and synthesising glycerides (Am. Journ. Phys., 1904, vol. 10, p. 191; Lewkowitsch-Chem. Tech. and Anal. of oils, fats and waxes, vol. 1, p. 97).

As to the mechanism of the reagent, it is most probably catalytic in nature. The action should be considered to be both physical and chemical. It is chemical as Lewkowitsch stated (Lewkowitsch-Chem. Tech. and Anal. of oils, fats and waxes, vol. 1, p. 89), not in the sense, that the reagent reacts with the oil, but in the sense that it decomposes in some way to set free acid in nascent state which accelerates catalytically on the hydrolysis of oils and fats. It is physical, because, besides the strong acid property possessed by the sulphonic acids and the mineral acid, it is really the physical character of the reagent of an oily nature, conferred by the introduction of higher hydrocarbons into the nucleus, thereby bringing the mutual solubility and the intimate contact of the molecules of oil and water that the splitting of the insoluble glycerides is effected.

It has been shown by Twitchell that with the solution of the same normality of HCl and naphthalene-stearo-sulphonic acid, soluble glycerides like triacetin can be saponified at about the same rate, due to the effect of the H-ions which are dissociated to about the same degree in solutions of the same strength. When it comes to the question of decomposing insoluble glycerides like oils and fats, dil. mineral acids like HCl or H₂SO₄ cannot effect this decomposition alone, unless coupled with the Twitchell reagent; as in the latter case, a heterogeneous system is obtained in which the oil layer and the acidulated water layer are separated, whereas in the case of soluble triglycerides, a homogeneous solution can be obtained. (Journ. Am. Chem. Soc., 1906, p. 196).

Further evidence is to be obtained when we compare that no change has occurred by passing steam through oil for two hours with 2% 60°Be H₂SO₄ alone, and that the action of hydrolysis proceeds to such an extent that more than 50% of the oil is decomposed in four hours when the Twitchell reagent is present. It is easily seen in carrying out these experiments, that with no reagent, the large oil globules are simply floating over water, while with the presence of the reagent and with only a suitable quantity of acid, the oil globules are so finely emulsified that a milky solution is obtained.

It is well known that catalysis in heterogeneous system can only proceed, provided that the required preliminary association of the reacting substances can take place freely. Suspension of such association will result in an effect similar to that observed in the presence of a catalyst poison; thus the condition, in the case of hydrogenation of unsaturated glycerides with palladium at a

temperature sufficiently low for the stearine produced to remain in a solid condition on the surface of the palladium, will gradually obstruct the free participation of the catalyst in the chemical change required. So is the case here too, if the association of the H-ions of the catalyst with the reacting system of the hydrolysing agent, water, and oil, does not take place freely as is brought about by the emulsification of the water and oil, the free participation of the reacting constituents in the desired chemical change will be obstructed.

To find an interpretation among the theories of catalysis which have been advanced, the adsorption theory would be the best, upon which the mechanism of the action of "Liquid Kontakt Saponifier" is capable of the simplest explanation. In this theory, it is assumed that, the reacting substrates are adsorbed on the enormous surfaces of some finely divided particles or colloids in the form of a film, so that the concentration of the reacting substrates is greatly increased and the rate of the reaction thereby accelerated.

This applies, in most cases, to the adsorption of gases or liquids on the surfaces of solids or colloidal particles; but remembering, that emulsion is a colloid, the disperse phase of which is also a liquid, there is no reason why the adsorption theory of catalysis could not apply in this case.

Now we have noticed, that the aqueous solution of the Twitchell reagent is colloidal, that it froths on shaking and that it possesses a detergent property just as a soap solution (U. S. P. 1,303,779 and 1,330,624).

From Hatschek's statement (Introduction to the Physics and Chemistry of colloids, p. 43) that frothing is a distinct indication that the dissolved substance lowers the surface tension of the solvent, and that the surface tension between water and fat is reduced by the presence of soap as shown by Donnon (Zeits. f. phys. Chem., p. 42-49, 1899), it is quite reasonable to assume, that the surface tension between oil and water in this process is also lowered by the presence of "Liquid Kontakt Saponifier."

By this lowering of surface tension between the two phases, emulsification of oil and water is greatly facilitated, as there is a close connection existing between the two (Hatschek-Introduction to the Physics and Chemistry of colloids, p. 43). Since the surface energy existing at the interface is the product of the area and its tension, thus:

Surface energy = Surface $\times$ Surface tension
(Taylor—The Chem. of colloids, p. 222), the surface must be greatly increased by the lowering of the surface tension or the process of emulsification.

Since the adsorptive power, which is based on the enormous surface development, is a property of the colloids or emulsoids, we naturally expect that, by this enormous increase of surfaces, the concentrations of the reacting substrates, oil and acidulated water, would be greatly increased by adsorption and the rate of the reaction thus promoted.

As a general theory of catalysis, which shall apply to every type of reaction, is probably impossible and as each reaction, and indeed, each catalyst employed for a given reaction, must receive special consideration with the object of setting up certain types of accelerating mechanism, the above consideration may serve as an explanation of the special type in question.

XI CONCLUSION AND SUMMARY

Results obtained in the foregoing paper in obtaining informations leading to a better knowledge of the working conditions governing the hydrolysis by Twitchell Process and in developing some means to shorten the time required, may be briefly summarized as follows:

(1) The general properties of the "Liquid Kontakt Saponifier" have been studied; and two other typical reagents along the line prepared and their activity studied. The "Liquid Kontakt Saponifier" is the most efficient among the three.

(2) Different factors influencing the rate of hydrolysis by this method have been systematically studied.

a. Mechanical stirring assists the rate of hydrolysis, though to a slight extent.

b. The extent of the hydrolysis increases with the time, but the rate falls off gradually.

c. The rate of hydrolysis increases with the % of the reagent used, but an amount higher than 1% seems to accelerate at the earlier stages and begins to slow down gradually towards the later stages; 3 or 5% causes foaming and persistent emulsion. Less than 1% effects hydrolysis very slowly. 1% is concluded to be the favorable quantity for most of the oils and fats so far studied. No discoloration of the fatty acids is increased by using a larger percentage of the reagent. The discoloration is mainly due to the effect of the air.

d. The influence of the acid seems to increase the discoloring effect of the air. Less than 1% of 60°Be H_2SO_4 gives light colored fatty acids; while with more than 1%, the discoloration effect becomes remarkable. With 1% of the acid, no discoloration effect will be produced if air is carefully excluded. Higher percentages of acid has a precipitating effect on the reagent and destroys the emulsion.

e. 100°C is the most favorable temperature for the process.

f. Percentage of water used at the beginning have no material influence on the splitting operation and no failure will result from using too much or too little water. For practical purpose, 40 to 50% is suggested.

g. Acid Wash assists the progression of the hydrolysis even with clean fatty materials, though to a very slight extent.

(3) Influence of a few of the neutral sulphates has been studied and found to give an inhibiting effect.

(4) Influence of the products of reaction has been studied; free fatty acids seem to accelerate the hydrolysis to a remarkable extent, whereas glycerine effects a reversible reaction and exerts a retarding effect.

(5) The "Liquid Kontakt Saponifier" has been improved and the process modified, by which two-thirds of the time required can be saved.

(6) The behavior towards the splitting operation of soy bean oil, sesame oil, cottonseed oil, cocoanut oil and mutton tallow has been studied. Cottonseed oil and soy bean oil are the difficultly saponifiable oils, while mutton tallow is the most easily saponifiable among the five.

(7) The action of the "Liquid Kontakt Saponifier" has been explained on the adsorption theory of catalysis and the nature of the reaction discussed.

NOTES

Notes on the determination of neutral fat and free fatty acids in a given sample—Acid value and saponification value.

This method is used to ascertain how far the saponification of an oil or fat has proceeded in the control of a technical saponification process in order.

The method as given by Lewkowitsch (Chemical Technology and Analysis of oils, fats and waxes, vol., 1 p. 636; 1913 Ed.) runs as follows:

"Take a conveniently large—not weighed—sample and determine in one and the same sample the number of cc normal alkali required for the neutralization and saponification values respec-

tively. Let a and b be the numbers found, then $\frac{a \times 100}{b}$ gives the proportion of free fatty acids."

Before testing for its accuracy, the operations in carrying out this determination and the meaning of the "Saponification value" must be clearly understood before the use of the formula, % fatty

acids = $\frac{a \times 100}{b}$ —can be properly used.

In carrying out this determination in one and the same sample, it is necessary to first titrate the free fatty acids in the alcoholic solution of the sample with standard alkali; here the number of cc of normal alkali for the ordinary determination of acid value is obtained. As the saponification value is to be determined in the same sample, alc. KOH must be then added as in the actual determination of the saponification value by heating on water bath or on asbestos board for half hour and titrating back the excess of alkali with HCl of known strength. Here the number of cc of normal alkali found is the number of cc of normal alkali required

for saponifying the neutral fat present and **not** for the determination of the saponification value i. e. for the **ester number** and **not** for the saponification number.

“The saponification number or value is the number of milligrams of KOH consumed in the **complete** saponification of 1 gm. of fat; or required to neutralise the **total** fatty acids in the sample, **whether free or in the form of esters.**” The ester number is the difference between the saponification number and the acid number and therefore shows the amount of alkali consumed in the saponification of esters or neutral fat.”

The above explanation and quotations are given for fear that one may easily just substitute the number of cc of normal alkali in determining the acid value for a, which is correct and the number of normal alkali in saponifying neutral fat for b which, in reality, should equal to the number of cc of normal alkali required for saponifying neutral fat + the number of cc of normal alkali for neutralizing the free fatty acids, (the acid value).

∴ a should equal to No. of cc of normal alkali required for the neutralization of the free fatty acids i. e. for the determination of acid value.

and b should equal to the No. of cc of normal alkali required for saponifying the neutral fat + that for the neutralization of free fatty acids i. e. for the determination of saponification value.

$$b = x + a;$$

For example; if the following actual sample of a mixture of fat and fatty acids were calculated according to $b = \text{No. of cc of normal alkali required to saponify the neutral fat only}$, then over 100% of fatty acids will be obtained which is impossible, whereas if calculated correctly as above mentioned the right % will be obtained.

The sample required 2.22 cc N KOH for neutralization of the free fatty acids i. e. for acid value, and 0.16 cc for saponifying the neutral fat. If 0.16 is substituted for b, then

$$\% \text{ fatty acids} = \frac{2.22 \times 100}{0.16} = 138.7$$

If correctly substituted, i. e. $b = 0.16 + 2.22 = 2.38$, then

$$\% \text{ fatty acids} = \frac{2.22 \times 100}{2.38} = 93.2.$$

The formula, $\% \text{ fatty acids} = \frac{a \times 100}{b}$, is simply derived

from the two other expressions for Acid value and Saponification value, thus

$$\text{Acid value} = \frac{\text{No. of mgms. KOH for Acid value}}{\text{wt. of sample taken}}$$

$$\text{Saponification value} = \frac{\text{No. of mgms. KOH for Sapn. value}}{\text{wt. of sample taken}}$$

$$\frac{\text{Acid value (free fatty acids)} \times 100}{\text{Sapn. value (combined and free fatty acids)}} = \% \text{ fatty acids}$$

$$= \frac{\text{No. of mgms. KOH for Acid value}}{\text{No. of mgms. KOH for Sapn. value}} \times \frac{\text{wt. of sample}}{\text{wt. of sample}} \times 100$$

$$\text{Therefore, \% fatty acids} = \frac{\text{No. of mgms. KOH for Acid value}}{\text{No. of mgms. KOH for Sapn. value}} \times 100$$

$$\text{i. e. \% fatty acids} = \frac{a \times 100}{b}$$

The above method is tested by determining the % fatty acids in the above mentioned way with a weighed sample.

(1) Calculation according to the above method, using a weighed sample.

Wt. of oil taken = 2.1019 gms.

cc of N. KOH required for Acid value = 0.1050

cc of N. KOH required for saponifying neutral fat = 7.1300

a = 0.1050

b = 7.1300 + 0.1050 = 7.2350

$$\% \text{ fatty acids} = \frac{0.105 \times 100}{7.235} = 1.45$$

(2) Calculation based on the same weight of sample and its Acid value and saponification value.

Wt. of the Sample	Acid value	Saponification value
2.1019 gms.	2.80	193.2

193.2 — 2.80 = 190.4 = neutral fat in the sample,

193.2 : 100 = 190.4 x ; x = 98.55 = % neutral fat,

100.00 — 98.55 = 1.45 = % fatty acids.

The agreement is therefore perfect.

AUTOBIOGRAPHY

I, Cheh-Yao Chang, was born in Show-Chow, Kwangtung, China, September 20, 1894. I received my secondary school education in the High Schools of Nanchang, Kiang Si and Peking; my undergraduate education at the Peking Government University, Peking, from which I obtained the Degree of Bachelor of Science in 1916. While in residence at Peking Government University I acted in the capacity of Assistant to Prof. Tung K. Yu from 1916 to 1917. In 1918, I obtained the Degree of Master of Arts from Cornell University, Ithaca, N. Y. In 1921, I completed all the requirements for the Degree of Doctor of Philosophy after a two years' residence, at the Ohio State University.

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